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ANALYTICAL ABSTRACTS

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No. 37 April, 1956

THE SOCIETY FOR ANALYTICAL CHEMISTRY

BULLETIN

FORTHCOMING MEETINGS

Ordinary Meeting of the Society, May 2nd, 1956

AN Ordinary Meeting of the Society will be held at 7 p.m. on Wednesday, May 2nd, 1956, in the Meeting Room of the Chemical Society, Burlington House, London, W.1.

The following paper will be presented and discussed:—

"The Composition of Some Deposits and Muds in Estuaries, Rivers and Lakes," by J. H. Hamence, M.Sc., Ph.D., F.R.I.C.

Joint Meeting of the Society with the Food Group of the Society of Chemical Industry, May 23rd, 1956

A JOINT Meeting of the Society with the Food Group of the Society of Chemical Industry will be held at 6.30 p.m. on Wednesday, May 23rd, 1956, in the Meeting Room of the Chemical Society, Burlington House, London, W.1.

Joint Meeting of the North of England Section, the Microchemistry Group and the Bradford Chemical Society, May 25th, 1956

A JOINT Meeting of the North of England Section, the Microchemistry Group and the Bradford Chemical Society will be held on Friday, May 25th, 1956. In the afternoon there will be a visit, by kind permission of the Coal Tar Research Association, to their laboratories at Gomersal, Leeds.

The subject of the evening meeting in **Bradford** will be "Microvolumetric Analysis."

Ordinary Meeting of the Scottish Section, May 11th, 1956

AN Ordinary Meeting of the Scottish Section will be held at 7 p.m. on Friday, May 11th, 1956, in the George Hotel, George Street, **Edinburgh**.

A lecture will be given on:—

"Complexones," by R. E. Stuckey, B.Sc., Ph.D., F.P.S., F.R.I.C.

Joint Meeting of the Physical Methods Group with the Photo-electric Spectrometry Group, May 25th, 1956

A JOINT Meeting of the Physical Methods Group and the Photo-electric Spectrometry Group will be held on Friday, May 25th, 1956, in **Oxford.**

The subject of the Meeting will be "Nuclear and Paramagnetic Resonance."

BRITISH STANDARDS INSTITUTION

DRAFT SPECIFICATIONS

A FEW copies of the following draft specifications, issued for comment only, are available to members of the Society, and can be obtained from the Secretary, The Society for Analytical Chemistry, 7-8 Idol Lane, London, E.C.3.

Draft Specifications prepared by Technical Committee FCC/4—Solvents and Allied Products.

CW(FCC)118—Draft B.S. for Diethyl Ether (Technical) (Revision of B.S. 579).

CW(FCC)119—Draft B.S. for *iso*Propyl Alcohol (Revision of B.S. 1595).

COMMUNICATIONS ACCEPTED FOR PUBLICATION IN *THE ANALYST*

THE following communications have been accepted for publication in *The Analyst*, and are expected to appear in the near future. It is not possible for the Editor to enter into correspondence about any of them.

"A Simplified Form of Coulometric Titration," by J. Hetman.

"The Determination of Deuterium by the Mass-spectrometric Method," by A. MacDonald and R. I. Reed.

"The Microbiological Assay of Inositol with a Strain of *Schizosaccharomyces pombe*," by F. W. Norris and A. Darbre.

"A Method for the Detection and Determination of Iodide in the Presence of Chloride," by M. Z. Barakat, M. F. Abd El-Wahab and M. M. El-Sadr.

"A Micro-scale Spot-test for Nicotine," by Policarpo Luis.

"Chromatographic Separation, Detection and Determination of Selenium," by E. G. Weatherley.

"The Determination of Non-fat Dry Milk Solids in Bread by Paper Chromatography," by H. Zentner.

"Paper Chromatography with Continuous Change in Solvent Composition. Part I: Separation of Fatty Acids; Part II: Separation of Surface-active Agents," by F. Franks.

"The Determination of Uranium by High-precision Spectrophometry," by A. Bacon and G. W. C. Milner.

"A Simple Colorimetric Method for Determining Blood Glucose," by N. Wahba, S. Hanna and M. M. El-Sadr.

"Factors Influencing the Polarimetric Determination of Lactose in Concentrated Whey Products," by M. A. House.

"The Volumetric Determination of Plutonium with Ethylenediaminetetra-acetic Acid," by G. W. C. Milner and J. L. Woodhead.

"Non-ferrous Metallurgical Analysis," by G. W. C. Milner. (Review.)

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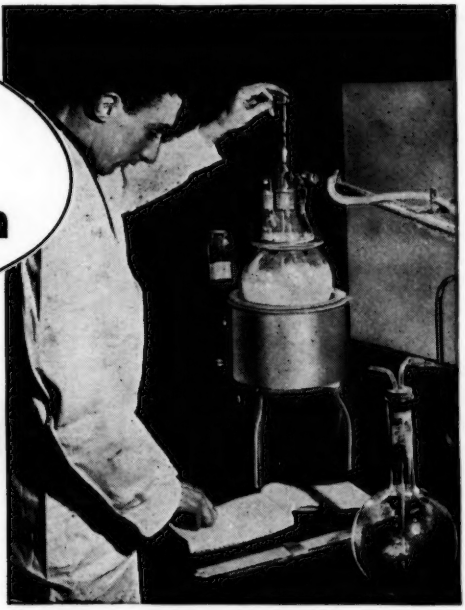
Incidental information

No. 9

items of interest from our laboratory notebooks



A modern touchstone.—***p*-Diethylaminobenzylidenerhodanine** will detect 0.2 microgram of gold in biological materials. (**Anal. Chem. 23,** 653 (1951).) Why look for gold in blood? Because rheumatoid arthritis is treated with gold compounds. Where does one obtain the reagent? From Hopkin & Williams Ltd. It is our Code 3769.5.

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Complexone chemistry bids fair to become a universal provider in analysis. Now we have ***o*-Cresolphthalein Complexone** ('Phthalein Complexone'), a compound of iminodiacetic acid and *o*-cresolphthalein, which forms coloured complexes with Mg, Zn, Ca, Sr and Ba. It is used as an indicator in the titration of the alkaline earths and zinc with sequestric acid. See **Helv. Chim. Acta 37,** 113 (1954). See also H & W Code 3525.

H&W

***o*-[2-(2-Hydroxy-5-sulphophenylazo)-benzylidene hydrazino] benzoic acid** has a long name, but it makes short work of the determination of zinc and copper when they are present together. It is just a matter of pH adjustment. The method is in **Anal. Chem. 26,** 1345 (1954). The reagent is on our 'Z' shelf (Z for 'Zincon'). H & W Code 9159.

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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

898. **The buoyancy of air in relation to analytical weighings.** H. Ulbricht. *Chemikerztg*, 1955, **79** (7), 201–205.—The effect of the buoyancy of air on the accuracy attainable with analytical balances is considered. Equations, diagrams, tables and numerical examples show the magnitude of the correction to be applied with varying densities of air, objects and weights. A. R. ROGERS

899. **Production of a slow and steady flow of hydrogen sulphide.** A. L. Harris and R. A. A. Taylor (Fuel Res. Stn., Greenwich, London). *Chem. & Ind.*, 1955, (46), 1471–1472.—A generator that gives a steady flow of H_2S at a desired rate is provided by dropping HCl (1:1) from a Mariotte's bottle (with a head large enough to overcome the max. pressure against which the gas has to be supplied) into a narrow funnel leading to a capillary tube, which passes to the bottom of a vessel containing a min. quantity of water and solid Na_2S. The rate of addition of the HCl is controlled by a screw-clip and observed in a drip sight-glass. S.C.I. ABSTR.

900. **Induced reactions in analytical chemistry.** A. I. Medalia (Boston Univ., Mass., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1678–1683.—Induced reactions can give rise to serious errors in both volumetric and colorimetric analysis based on oxidation - reduction reactions; they are different from catalytic reactions in that they participate in the primary reaction. Two types of reaction are considered: (*i*) *coupled reactions* in which substance *A* (*actor*) reacts with both *B* (*inductor*) and *C* (*acceptor*) in a fixed ratio, and (*ii*) *chain reactions* in which the actor *A* reacts only with the acceptor *C*. Examples are given. D. G. HIGGS

901. **Rapid method of reducing silver.** P. P. Shat'ko (Dnepropetrovsk Med. Inst.). *Zavod. Lab.*, 1955, **21** (8), 921.—Silver can be recovered from residues by means of $CrCl_2$ or $CrSO_4$ solution, which reduces AgCl to Ag. Inorganic residues are converted into AgCl, which is left in contact with the Cr^{++} solution for 5 to 10 min. The pptd. Ag is washed with water to remove Cl' then dissolved in HNO_3 (1 + 1) and the soln. is evaporated to give crystals of $AgNO_3$. Organic residues are treated with $KMnO_4$ and H_2SO_4. The solution is evaporated to fumes and AgCl is pptd. after addition of water and HCl. G. S. SMITH

902. **Preparation of carbonate-free solutions of strong bases.** D. M. G. Armstrong (Royal Veterinary College, London). *Chem. & Ind.*, 1955, (44), 1405–1406.—A solution of KOH of suitable concn. (*e.g.*, 0·5 *N*) is treated with excess of $Ba(OH)_2$ to precipitate CO_3'' as $BaCO_3$ and is then passed through a sintered-glass filter into a column of resin of sulphonic acid type (*e.g.*, Zeo-Karb 225, prepared by elution with KNO_3), exchanging Ba^{++} for K^+. The resulting solution is led away through polyethylene tubing into a collecting bottle closed by a rubber bung fitted with two glass tubes, one of which extends to the bottom of the bottle and carries the solution, whilst the other is connected to a filter pump. S.C.I. ABSTR.

903. **Sodium tetraphenylboron, 1949–1955: A comprehensive bibliography.** A. J. Barnard, jun. (J. T. Baker Chemical Co., Phillipsburg, N.J., U.S.A.). *Chemist Analyst*, 1955, **44** (4), 104–107.—A comprehensive bibliography has been arranged chronologically. (85 references.) O. M. WHITTON

904. **Use of thiosemicarbazones as reagents in inorganic analysis. II.** G. N. Mitra and S. S. G. Sircar (Ravenshaw College, Cuttack, India). *J. Indian Chem. Soc.*, 1955, **32** (7), 435–441.—The investigation of a further series of thiosemicarbazones of eight aldehydes and ketones (*cf. Anal. Abstr.*, 1955, **2**, 30) is described. Benzylidene-, anisylidene- and salicylidene-acetone derivatives were found to be highly sensitive (1 in 10^7 dilution) for the quant. estimation of Cu, Co and Ni. The nickel ppt. is slightly sol. in water, so washing should be restricted. H. B. HEATH

905. **Vanadyl acetate, a new volumetric reagent for titration in glacial acetic acid.** J. Novotný (Karlovy Univ., Prague, Czechoslovakia). *Chem. Listy*, 1954, **48** (12), 1865–1867.—A 0·1 or 0·05 *M* soln. of vanadyl acetate in glacial acetic acid can be used as a reagent for polarometric titrations. With CrO_3 the following reaction occurs—

$$3\,VO(CH_3COO)_2 + CrO_3 \rightleftharpoons 3\,VO_2(CH_3COO) + Cr(CH_3COO)_3;$$

1 ml of a 0·05 *M* soln. of vanadyl acetate is thus equivalent to 1·6668 mg of CrO_3. To prepare the reagent, NH_4VO_3 (23·4 g) is ignited, the resulting oxide is mixed with powdered oxalic acid dihydrate (12·6 g) and glacial acetic acid (48 g), and the mixture is heated on a water bath at 70° C, with constant stirring. A lively reaction occurs with evolution of CO_2, and the mixture turns blue - green. The reaction product is dissolved in glacial acetic acid (100 ml) and the soln., which is stable, is standardised manganometrically. G. GLASER

906. **Thermogravimetry.** C. Barcía Goyanes. *Inf. Quím. Anal.*, 1955, **9** (5), 159–174.—Applications of thermogravimetric methods in analysis and various types of thermobalances are described. L. A. O'NEILL

907. **Fluorescent acid - alkali indicators.** G. N. Kosheleva (Inst. Chem. Reagents). *Zavod. Lab.*, 1955, **21** (8), 900–906.—A review is presented with tabulated data and 55 references. G. S. SMITH

908. **Preparation of decinormal standard solutions of acid from alkali sulphate, nitrate or chloride by means of cation-exchange resin.** Shizo Hirano and Moriji Kurobe (Nagoya Univ., Chigusa-ku, Nagoya). *Japan Analyst*, 1955, **4** (6), 379–383.—A known amount of sulphate, nitrate or chloride of Na, K or ammonium is passed through a column of Amberlite IR-120 (diameter, 32 mm; length, 400 mm) (at <4 ml per min.), washed with water and made up to a definite volume. The product can be used for the standardisation of alkali soln. The quality of the resin must be carefully tested before use. This method decreases the time taken for the prep. of standard mineral acid (<1·5 hr. for 1 litre). K. SAITO

909. **The scope and applicability of pH titration.** H. Röpke and W. Neudert (Schering A.-G., Müllerstrasse 170, Berlin, Germany). *Z. anal. Chem.*, 1955, **148** (4), 241–249.—A review is given of the uses of pH titration, including determination of equivalent pH values, equivalent weights, pH values, and concentrations of single substances and mixtures. Greater use of the technique is expected with the development of automatic titration apparatus. A. R. ROGERS

910. **Potassium rhodizonate as an indicator in argentimetric titrations.** J. P. Mehlig (Oregon State College, Corvallis, U.S.A.). *Chemist Analyst*, 1955, **44** (4), 87–89.—The application of potassium rhodizonate to the argentimetric titration of bromides, iodides and cyanides and to the Volhard titration of silver nitrate with potassium thiocyanate is described. The results are compared with those obtained by the use of chromate and ferric alum as indicators. In argentimetric titrations, the average difference between the rhodizonate method and the chromate and ferric alum methods was 0·07 per cent. The percentage error ranged from −0·28 to + 0·17. The precision for rhodizonate was ± ±0·11 per cent. O. M. WHITTON

911. **Potentiometric titrations involving chelating agents, metal ions and metal chelates.** S. Siggia, D. W. Eichlin and R. C. Rheinhart (General Aniline & Film Corp., Easton, Pa., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1745–1749.—It is shown that, by varying the solvents, the pH and especially the electrode system, a number of metals can be titrated potentiometrically with chelating agents and *vice versa*. The three chelating agents investigated were EDTA (**I**), nitrilotriacetic acid (**II**) and NN-di(β-hydroxyethyl)glycine (**III**). **I** was found to exhibit strong chelating properties with all the metals studied and gave sharp potential breaks; **II** gave sharp breaks for Cu, Zn and Pb, whilst **III** showed relatively poor properties under the conditions tried; only Cu and Pb showed promise. Conditions, metal ion and electrode systems can be varied, so that mixtures of chelating agents can be determined. D. G. HIGGS

912. **Coulometric titrations with electrolytically generated uranous ion.** W. D. Shults, II, P. F. Thomason and M. T. Kelley (Oak Ridge National Lab., Tenn., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1750–1751.—Dilute solutions of both $Ce(SO_4)_2$ and $K_2Cr_2O_7$ can be accurately titrated with $U^{\cdots\cdot}$ generated electrolytically with constant current at a platinum cathode immersed directly in the sample soln. containing 0·2 *N* uranyl sulphate in 0·5 *N* H_2SO_4. The end-point is detected with a platinum wire - S.C.E. system, the electrolysis time being measured automatically. The cut-off potentials are 0·88 V for Ce^{IV} and 0·18 V for Cr^{VI}, both *vs.* the S.C.E. Since rapid and large (300 to 500 mV) changes of potential occur at the end-points, the electrolyte is first brought to the cut-off potential before the sample is titrated. W. J. BAKER

913. **Conductimetric titration with a photoelectric colorimeter.** M. I. Kulenok (Leningrad Pediatric Medicinal Inst.). *Zavod. Lab.*, 1955, **21** (9), 1027–1029.—In the solution to be titrated are immersed within a shield two platinum-disc electrodes, the distance between which can be varied in a vertical direction. The electrodes are connected in series with the lamp of a photocolorimeter and during a titration act as a rheostat. The photocurrent read on the galvanometer is proportional to the third power of the change of the voltage of the current to the lamp. The principle of conductimetric titration based on this scheme is applicable to many types of reaction. G. S. SMITH

914. **Use of nomographic methods of calculation in spectrographic analysis.** R. N. Rubinshteĭn and N. G. Karpel'. *Zavod. Lab.*, 1955, **21** (9), 1094–1103.—A number of nomographic methods applicable to spectrographic analysis are described. G. S. SMITH

915. **The effect of the form of combination of elements in the spark spectrographic analysis of solutions.** A. B. Shaevich (Lab. Standard Samples Ural Inst. Ferrous Metals). *Zavod. Lab.*, 1955, **21** (9), 1089–1094.—Experiments carried out on the spectrographic examination of the residues after evaporation of solutions of alloy steel in various acids show different calibration curves. The difference is most marked between sulphate solutions and chloride and nitrate solutions. G. S. SMITH

916. **A study of matrix effects on a graphite base semi-quantitative [spectrometric] procedure.** E. L. Grove and J. A. Norris (Oak Ridge National Lab., Tenn., U.S.A.). *Applied Spectroscopy*, 1955, **9** (2), 63–68.—A general method is described for the analysis of electromagnetically separated isotopes and miscellaneous samples for impurities. Samples are mixed in the ratio of one part to nine parts of graphite by weight, loaded into a narrow-crater type of electrode and arced in a 5-amp. high-voltage a.c. arc. Occasional erroneous analyses are attributed to inter-element effects, and investigations into the magnitude and nature of these are described. In particular the effects of various alkali and alkaline-earth salts on the spectra of Fe, Al and Ba have been studied. P. T. BEALE

917. **Identification of short-lived species in chemical reactions. Use of flash photolysis and rigid "glassed" solvents in identification and rate studies of reaction intermediates.** E. W. Abrahamson (State Univ. New York, Syracuse, N.Y., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1695–1698.—The three types of intermediate short-lived species that take part in chemical reactions are discussed—(*i*) molecular (or ionic) complexes, which occur, for example, in enzyme reactions; (*ii*) atoms and free radicles, usually associated with chain reactions; and (*iii*) atoms or molecules in excited states, usually associated with free-radicle reactions. Intermediates of type (*i*) are best studied by "flow"

techniques, and those of types (*ii*) and (*iii*) by flash photolysis, which generates the intermediates in concentrations sufficiently high for physical properties, such as absorption spectra, to be investigated. This generation is effected by the rapid introduction of large amounts of light energy into the system, and involves the triggered discharge of energy stored in a capacitor across a large spark gap. Another method of obtaining high concentrations of short-lived species is the irradiation of reactants dissolved in rigid "glassy" solvents, *e.g.*, a mixture of ether, *iso*pentane and alcohol frozen at the temp. of liquid nitrogen. The molecules of reactant split into radicle or ionic fragments, which remain stabilised in a condition suitable for studying their absorption spectra.

D. G. HIGGS

2.—INORGANIC ANALYSIS

918. **Qualitative scheme for heavy metals based on colorimetric micro tests.** M. R. Lardera and A. Mori (Lab. Ric. Montecatini, Terni, Italy). *Ann. Chim., Roma*, 1955, **45** (9–10), 869–886.—A scheme for the detection of traces of heavy metals in organic materials, particularly fibres and synthetic resins, is described. The material is destroyed in a Carius tube and the resulting nitric acid solution of the metals is treated in three portions: (*a*) with dithizone in $CHCl_3$ at various pH values (0·5 to 1, 3·5, 8 to 9) to extract successively Hg, Ag, Cu, Co, Pb, Bi, Zn, Cd and Ni, and leave Ti, W, V and Mo in the aq. phase; (*b*) with Zn and H_2SO_4 to separate As and Sb as the volatile hydrides; (*c*) with anhydrous HCl, removing Sn as volatile $SnCl_4$ and extracting $FeCl_3$ and $HAuCl_4$ with ether, leaving Al, Cr, Mn and Pt in the residue. Tests for the individual metals in the fractions are outlined and the sensitivities indicated.

L. A. O'NEILL

919. **New methods for the separation of cations by paper chromatography.** G. Stefanović, T. Janjić and R. Crnojević (Inst. Chem., Belgrade, Yugoslavia). *Bull. Soc. Chim. Belgrade*, 1955, **20** (5), 343–348.—Some previous methods of separating cations by paper chromatography have been confirmed. Sharper separations are obtained with the solvents described below. Ascending chromatography on Whatman No. 1 paper is used with a solvent movement of 30 cm in 21 hr. R_F values of 0·97, 0·74 and 0·63 are found for $Fe^{\cdots}$, $Al^{\cdots}$ and $Cr^{\cdots}$, respectively, in a soln. of 4 g of NH_4SCN in 20 ml of 2 *N* HCl mixed with 20 ml of methanol and 60 ml of *n*-propanol. R_F values of 0·61, 0·39 and 0·75 are found for $As^{\cdots}$, $Sb^{\cdots}$ and $Sn^{\cdot\cdot}$, respectively, in a soln. of 4 g of tartaric acid in 20 ml of water mixed with 20 ml of *n*-butanol.

A. B. DENSHAM

920. **Chloramine B as a volumetric reagent. Determination of metals.** Apar Singh (Punjab Univ. Coll., Hoshiarpur, India). *J. Indian Chem. Soc.*, 1955, **32** (7), 473–478.—The use of chloramine B (**I**) for the quantitative estimation of Cu, Hg, Zn, Cd and Bi is described, the procedure adopted being that previously reported (*Anal. Abstr.*, 1955, **2**, 2019). Copper is pptd. as $Cu_2(SCN)_2$ or as $Cu[Hg(SCN)_4]$; Hg is pptd. as Hg_2Cl_2 or as $Hg[Zn(SCN)_4]$; and Zn as $Zn[Hg(SCN)_4]$; then in all instances the washed ppt. is treated with ICl in the presence of conc. HCl and the liberated I is titrated against a standard soln. of **I**. Cadmium is determined either by pptn. as the 5:6-benzoquinoline salt of cadmium hydriodide, the I in the ppt. being titrated with standard **I**, or as cadmium oxinate by pptn. with 8-hydroxyquinoline, the oxine in the ppt. being brominated with excess of KBr in the presence of standard **I** (*cf. Anal. Abstr.*, 1955, **2**, 1253). Bismuth is determined as the oxinate or as the 8-hydroxyquinoline salt of bismuth hydriodide, the I in the ppt. being titrated with standard **I** in the presence of HCN.

H. B. HEATH

921. **Use of aryloxy fatty acids in inorganic analysis.** S. K. Datta (Darjeeling Gov. Coll., India). *Naturwissenschaften*, 1955, **42** (15), 439.—Phenoxyacetic acid was used by Datta (*J. Indian Chem. Soc.*, 1950, **27**, 358) for the determination of mercuric and mercurous mercury from acid solution. The author has prepared *o*-nitrophenoxy-, *o*- and *p*-tolyloxy-, β-naphthyloxy-, guaiacyloxy-, thymyloxy-, 2-formylphenoxy- and 2-carboxyphenoxyacetic and -propionic acids. Some of these acids may be used for the determination of Hg, Fe, Th, Zr and U; Th, Zr and U may be separated from each other by control of hydrogen-ion concentration of the mixture. The determination is a gravimetric one; details will be published later.

E. KAWERAU

922. **Continuous detection of hydrogen or hydrogenous materials in gases.** L. P. Pepkowitz (General Electric Co., Schenectady, N.Y., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1805.—A hygrometric instrument for the continuous detection and determination of low concn. of hydrogen, or hydrogen-containing substances, in the inert blanket-gases used in nuclear reactors is described. Except for the vertical copper oxide furnace-tube heated to between 350° and 400° C, in which the hydrogen is converted into H_2O, the apparatus is almost identical with the continuous oxygen-analyser (*Anal. Abstr.*, 1955, **2**, 1975). The concn. of hydrogen is calculated from the dew-points of the gas after by-passing and passing through the copper oxide furnace, respectively. The sensitivity is 0·001 per cent. (by vol.), positive responses being attained within 5 sec.

W. J. BAKER

923. **Probable mechanism of the Karl Fischer titration: modification of reagent and method.** E. Bonauguri and G. Seniga (Ist. Chim. Ind. Univ. Milan). *Ann. Chim., Roma*, 1955, **45** (9–10), 805–817.—To investigate the limitations of the Karl Fischer method for the determination of H_2O, the effect of methanol, excess SO_2 and the titration products, particularly $C_5H_5N.SO_3$, on the reaction have been examined. As a result of the findings the following modifications are proposed: (*a*) substitution of dioxan for methanol in the standard solution and where necessary as solvent or diluent for the sample; (*b*) modification of the reagent to a ratio of $I:SO_2$:pyridine:methanol of 1:2:9:16. Under these conditions it is possible to determine the exact content of H_2O of the standard solution from titrations of the standard and of the dioxan, thereby simplifying the procedure. Some results on citric and oxalic acids, Na acetate and tartrate, and brucine are quoted.

L. A. O'NEILL

924. **The determination of the alkali metals by flame photometry.** E. Pungor and E. É. Zapp (Inst. Inorg. and Anal. Chem., L. Eötvös Univ., Budapest). *Acta Chim. Acad. Sci. Hung.*, 1955, **7** (1–2), 185–198.—The spectrophotometric determination of the alkali metals is carried out in the presence of each other and in the presence of various

anions. The alkali metals are present in an aq. soln. of their chlorides, and the anions either as the acid or as the ammonium salt. The presence of the more easily ionisable K, Rb and Cs does not affect the emission of Li and Na, nor do the Li and Na interfere in the emission of the other three metals. Large deviations, however, occur when K, Rb and Cs are determined in the presence of each other. This effect is ascribed to the high concn. of electrons in the flame area. Whilst the effect of H_2SO_4 is negligible, $(NH_4)_2SO_4$ and $(NH_4)_3PO_4$ cause interference by the formation of acid salts.

J. H. WATON

925. **The determination of rubidium and caesium in sodium - potassium alloys and related materials by radioactivation.** M. J. Cabell and A. Thomas (Atomic Energy Research Estab., Harwell, England). A.E.R.E. C/R 1725, 1955, 10 pp.—An extension of the method of Smales and Salmon (*Anal. Abstr.*, 1955, **2**, 1141) for the determination of Rb and Cs in sea water and related materials by radioactivation is described. The introduction of a step involving the separation of the alkali metals by cation-exchange chromatography has made it possible to determine Rb and Cs accurately in the presence of large amounts of K and Rb, respectively. The separation is effected on a column of Zeo-Karb 315 (< 80 mesh), similar to that described by Kayas (*J. Chim. Phys.*, 1950, **47**, 408), from which K and Na can be eluted in separate fractions with 0·1 *N* HCl, and Rb and Cs with 1·0 *N* HCl. The Rb may be obtained in a day and the Cs can then be eluted overnight. Automatic fraction-collecting is unnecessary and several separations can be carried out simultaneously by a single operator. After conversion into the chloroplatinates, the Rb and Cs are counted for β, γ-activity, with an end-window Geiger counter. The application of the method to the analysis of Na - K alloys and to KOH and KCl is described in detail.

K. A. PROCTOR

926. **Note on separation of copper by aluminium.** R. S. Young (Internat. Nickel Co. of Canada, Ltd., New York). *Chemist Analyst*, 1955, **44** (4), 98–99.—In the quant. separation of Cu from solutions containing Co and Ni, by the use of Al, long boiling in 10 per cent. H_2SO_4 is generally required to ppt. the Cu. The ppt. must be washed very thoroughly to remove adsorbed salts, and the complete separation of Cu must be verified by insertion of a fresh surface of Al. The small quantities of Co and Ni remaining in the pptd. Cu do not interfere in its electrolytic or iodimetric determination.

O. M. WHITTON

927. **Amperometric titration of copper with rubeanic acid.** A. K. Zhdanov, V. A. Khadeev and O. K. Vyakozina (Central Asia State Univ.). *Zavod. Lab.*, 1955, **21** (8), 913–916.—Rubeanic acid shows two polarographic waves. The first is well defined and has a half-wave potential *vs.* the S.C.E. of 0·470 V in 0·1 *M* sodium acetate and 0·750 V in aq. *M* NH_3 soln. The half-wave potentials of the second wave are 0·930 and 1·5 V, respectively. The amperometric determination of Cu with rubeanic acid can be carried out at 0·3 V. Large amounts of SO_4'', NO_3', acetate, Zn, Pb, Al, Cd or Mn have no effect on the titration. Large amounts of Cl' interfere. Small amounts of Co, Ni and Cr do not interfere. Ions of Fe^{II} and Fe^{III} are harmful, but Fe^{III} up to 0·01 *M* can be tolerated if just enough tartrate is added to form a complex. To determine Cu in brass, 0·2 g is dissolved in 5 ml of conc. HNO_3, 20 ml of water are added, the soln. is boiled to remove oxides of N, 2 *N* NaOH is added until the soln. is slightly acid, then the soln. is made up to 250 ml and 25 ml are taken. To determine Cu in duralumin, 1 g is dissolved in 30 ml of 20 per cent. NaOH, 30 ml of H_2SO_4 (1 + 5) and 6 ml of conc. HNO_3 are added, and the soln. is boiled to dissolve the Cu. Sodium hydroxide is added until a cloudiness appears, the soln. is made up to 250 ml and 25 ml are taken. In either case sodium acetate soln. is added to give a 0·1 to 1 *M* soln. and also methylene blue as max. suppressor. With duralumin, 0·5 ml of tartrate soln. (concn. not given) is added. Oxygen is removed by the passage of H and the Cu is titrated at 0·3 V with rubeanic acid (concn. not stated) in acetic anhydride, in which it is more sol. and more stable than in ethanol.

G. S. SMITH

928. **Polarographic determination of copper, iron, cadmium and lead in zinc.** J. Doležal and P. Hofmann (Karlovy Univ., Prague, Czechoslovakia). *Chem. Listy*, 1955, **49** (1), 47–50.—The polarographic behaviour of Cu, Fe, Cd and Pb in solutions containing 0·8 *M* ethylenediamine tartrate and 0·08 *M* $K_4P_2O_7$ in the presence of a large excess of Zn was studied, and the results were adapted to the simultaneous determination of Cu, Fe, Cd and Pb in Zn, zinc powder and alloys. *Procedure*—Dissolve the sample of Zn (5 g for samples containing from 0·05 to 2 per cent. of the metallic impurities, 1·6 g for samples with >2 per cent.) in sufficient HCl containing a few drops of HNO_3, and dilute the soln. to 100 ml. Neutralise a 5-ml aliquot with aq. NaOH until turbidity begins to form, add 2 *M* ethylenediamine tartrate (10 ml) and *M* $K_4P_2O_7$ (2 ml), adjust the acidity to a pH of 6 to 7, dilute to 25 ml and polarograph from 0 V in an atmosphere of nitrogen.

G. GLASER

929. **Chemical analysis by the use of catalysed or induced reactions. VI. Micro-determination of copper, cobalt and iron by reflectance spectrophotometry.** Shukichi Sakuraba (Shizuoka Univ., Oiwake, Hamamatsu). *Japan Analyst*, 1955, **4** (6), 372–376.—Small amounts (<50 μg) of Cu and Co^{II} (and Fe^{III}) are co-pptd. with Zn (30 to 40 mg) by $(NH_4)_2Hg(SCN)_4$ (30 per cent., 4 ml) at pH 2 to 4·5 at room temp.; the ppt. show characteristic colours. When the reflectance of the dried ppt. is measured at a certain wavelength (Cu, 500 mμ; Co, 605 mμ), the ratio of the absorption coeff. to the scattering coeff. is proportional to the content of Cu or Co. The amounts of the reagents and the temp. at which the ppt. is produced influence the result. Both Co and Cu are determined in a mixture with a standard deviation less than $\pm$2·1 per cent. (for Cu alone, 1·37 per cent.). Ferric iron is similarly determined in the absence of other coloured ions.

K. SAITO

930. **The use of dithionite as a separating agent in metal analysis. I. Separation of copper in iron and steel.** Hiroshi Kitagawa and Norio Shibata (Hitachi Central Res. Lab., Kokubunji, Tokyo). *Japan Analyst*, 1955, **4** (6), 358–361.—Copper is pptd. with dithionite from an H_2SO_4 soln. (<1 *N*), in the presence of a large amount of Fe, as a mixture of metallic copper and the sulphide. Arsenic, Mo, Te, Se, Sn and Sb are also pptd. as sulphides. The greater the concn. of the acid and the higher the temp. at which the ppt. is produced, the higher is the content of CuS in the ppt. The sample (1 to 3 g) is dissolved in dil. H_2SO_4 (1 + 5, 50 ml) and

diluted to 200 ml. After boiling for 1 min. with dithionite (1 g), the ppt. is ignited to convert all the Cu into oxide, which is dissolved in HNO_3 and iodimetrically determined. K. SAITO

931. **A rapid method for the determination of copper in blast-furnace slag.** Sasiti Ikeda (Nippon Mining Co., Saganoseki, Oita-ken). *Japan Analyst*, 1955, **4** (7), 431–434.—The colour of iodine, resulting from the interaction of Cu with KI in an acetic acid soln., obeys Beer's law in the range 2·5 to 5 mg of Cu per 200 ml. The influence of $Fe^{\cdots}$ is excluded by the addition of NH_4F (1 g for 30 per cent. of Fe in the sample). *Procedure*—The sample (1 g) is heated with HNO_3 (1 + 3, 10 ml) and H_2SO_4 (1 + 3, 5 ml) for 5 min., and then with HF (5 ml) until white fumes are evolved. The product is diluted with water, made alkaline with aq. NH_3 soln., and acetic acid (1 + 1) is added until an excess of 3 ml is present. Ammonium fluoride soln. (10 per cent., 10 ml) and KI (5 g) are added and the soln. is made up to 200 ml. The product is filtered through a dry filter-paper and its extinction is measured at 420 mμ. The time taken for an estimation is reduced (≃17 min.) by dissolving the sample (1 g) in HNO_3 (1 + 1, 15 ml) and HF (5 ml) and by decomposing the excess of nitrous acid with urea (1 g). K. SAITO

932. **Electrolytic method of obtaining analytical concentrates for the determination of impurities in copper.** A. K. Babko, P. V. Marchenko and T. N. Nazarchuk (Inst. Gen. Inorg. Chem., Acad. Sci., Ukraine SSR). *Zavod. Lab.*, 1955, **21** (6), 662–664.—The method is based on the simultaneous anodic dissolution of the sample and the cathodic deposition of Cu in Hg. Mercury (100 g) is placed in a 200-ml beaker with 50 ml of water, 1 ml of H_2SO_4 and 1 ml of HNO_3. A connection to the Hg is made through a platinum wire in a glass tube. The sample of copper, 10 g of plate or rod, is suspended in the solution. A current of 2 to 5 amp. is passed for 4 hr.; about 3 to 4 g of the sample dissolves. The sample is washed and weighed, the difference being taken as the sample weight. A platinum anode is inserted and the electrolysis is continued for 30 min. to remove Cu from the solution. The amalgam is shaken for 30 min. with a dil. copper salt solution. Tin, Pb and Bi are completely extracted from the amalgam and can be determined colorimetrically. With Pb, the latter part of the electrolysis can be omitted since Pb does not enter the amalgam while copper salts are present. Nickel, Sb and Fe cannot be completely extracted from the amalgam. A platinum cathode is used instead of Hg and the electrolyte contains 2 ml of HNO_3 and 1 ml of H_2SO_4 in 50 ml of water. The sample is dissolved completely, a platinum anode is inserted and the electrolysis is continued until the solution is colourless. Traces of Cu are removed with H_2S prepared from Na_2S, and Fe and Ni are determined in the filtrate. G. S. SMITH

933. **Anodic iodide method of amperometric determination of silver.** O. A. Songina (Kazakh State Univ.). *Zavod. Lab.*, 1955, **21** (6), 665–669.—Experiments on the anodic oxidation of I' with a rotating platinum electrode are described. Oxidation starts at +0·55 V *vs.* the S.C.E. independently of the pH within the range 6 to 10. For the amperometric determination of Ag, a potential of +1·0 V is recommended. No interference is given by Cu, Fe, Pb and Zn. G. S. SMITH

934. **Detection of gold (III) in non-aqueous solution.** P. W. West and T. C. McCoy (Coates Chem. Lab., Louisiana State Univ., Baton Rouge, La., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1820–1821.—The test consists in saturating 2 drops of the sample (aq. soln.) with KCl at pH 2 to 6, extracting the chloroauric acid into *n*-butanol (1 to 2 ml) and then adding 1 drop of 1 per cent. 1-naphthylamine in *n*-butanol; an intense violet colour within 2 or 3 min. indicates the presence of gold. The limit of detection is 1 μg; $Hg^{\cdot}$ and CrO_3'' interfere, but can be controlled; CN' repress the reactions.

W. J. BAKER

935. **Volumetric method for the determination of gold.** C. B. Riolo and E. Garrini (Ist. Chim. Gen. Univ., Pavia). *Ann. Chim., Roma*, 1955, **45** (9–10), 767–772.—The metal, as aq. $AuCl_3$, is treated with $NaClO_2$, and the ClO_2 liberated, according to the reaction $AuCl_3 + 3NaClO_2 \rightarrow Au + 3NaCl + 3ClO_2$, is carried over by an inert gas (CO_2), and absorbed in weakly acidified aq. KI (≃1 per cent.); the I liberated is determined by titration. The apparatus consists of a train of Drechsel bottles. The reaction is allowed to proceed for ≃15 min. before starting the gas stream, which is continued for ≮1 hr. Other metals, including Cu, Ag, Zn, Ni, Pt and Cd, do not interfere.

L. A. O'NEILL

936. **Chemical analysis of beryllium. XVI. Separation of beryllium from aluminium and iron by means of ammonium carbonate and basic acetate.** Tomoyuki Akiyama (Kyoto College of Pharmacy, Higashiyama-ku, Kyoto). *Japan Analyst*, 1955, **4** (7), 417–420.—Hydroxides of Fe^{III} and Al are pptd. with ammonium carbonate. The ppt. is filtered off and dissolved in dil. HCl and the pptn. is repeated three times; Be is pptd. from the combined filtrates with aq. NH_3 soln. In the presence of Mn^{II}, both Fe and Mn are pptd. as sulphides, and Al in the filtrate is pptd. with ammonium carbonate. When basic acetates of Fe, Al and Be are extracted with $CHCl_3$, only Be acetate dissolves and is thus separated from Al and Fe.

K. SAITO

937. **New oxidimetric method for determination of small quantities of magnesium with 8-hydroxyquinoline.** R. Wojtas (Faculty of Agric. Chem., Cracow, Poland). *Przem. Chem.*, 1954, **10** (10), 540–542.—After the usual treatment of the ore, the magnesium present in limestone or dolomite is pptd. by a 2·5 per cent. soln. of 8-hydroxyquinoline. The ppt. is dissolved in H_2SO_4 (1:10) and the soln., while hot, is titrated with 0·1 *N* $KMnO_4$. The error is 0·5 per cent. for 0·5 to 20 mg of Mg and up to 5 per cent. for 0·02 mg of Mg. The method is said to be as rapid and reliable as the colorimetric 8-hydroxyquinoline method and is not affected by the presence of small quantities of Fe and Al. Its adaptation for the determination of Mg in water, soil and plants is to be studied.

A. O. JAKUBOVIC

938. **Compleximetric method of determining magnesium in carnallite salts and ores containing boron.** V. A. Kazarinova-Oknina (State Sci. Res. Inst. Mineral Raw Materials). *Zavod. Lab.*, 1955, **21** (6), 644–646.—For the determination of Mg and Ca in carnallite, the solution at pH 12 is titrated with EDTA (disodium salt) (**I**), with murexide as indicator, to give the content of Ca. Another portion is titrated, with Eriochrome black T as indicator, to give the sum of Ca and Mg; Mg is obtained by

difference. For the determination of Ca and Mg in borate ores, the ore is extracted with HCl, and 25 to 50 ml of the solution containing 1 to 30 mg of Ca and Mg are treated with aq. NH_3 to ppt. the sesquioxides, and the solution is filtered. The solution is evaporated to a suitable volume and Ca and Mg are determined as described above. For the determination of Ca and Mg in the presence of phosphate, *e.g.*, in apatite, Ca is determined first by decomposing 0·5 g of apatite with 10 ml of HCl (1 + 1), diluting to 250 ml, taking a 50-ml aliquot portion and adding to it 25 ml of 0·1 *N* **I**; NaOH solution, 10 to 20 per cent., is added to give a pH of 12 (universal indicator), and then 0·2 to 0·3 g of murexide indicator. The excess of **I** is determined by titration with 0·1 *N* $CaCl_2$. Under the same conditions, 25 ml of **I** solution are titrated with the $CaCl_2$ solution. The result is calculated to Ca. The total Ca and Mg is determined by adding 25 ml of 0·1 *N* **I** to 50 ml of the acid extract, adding 10 ml of a buffer solution (prepared by dissolving 67 g of NH_4Cl in water, adding 570 ml of 25 per cent. aq. NH_3 solution and diluting to 1 litre), and 8 to 10 drops of Eriochrome black T indicator. The solution is diluted to 100 ml and carefully titrated with 0·1 *N* $MgSO_4$. Under the same conditions, 25 ml of **I** solution are titrated with the $MgSO_4$ solution.

G. S. SMITH

939. **The effect of some sample forms on the reproducibility of spectrographic analysis of certain magnesium alloys using pin electrodes and a simple source unit.** E. C. Mills and S. E. Hermon (High Duty Alloys, Ltd., Slough, England). *Metallurgia*, 1955, **52**, 210–212.—The following samples were used—die-cast pencils made in 8-pin and 4-pin dies, extruded rod, machined pencils, and vertically and horizontally cast die-cast discs. The alloys used covered the following composition ranges—Al, 7 to 11; Zn, <1·0; Mn, <0·4; Si, <0·3; and Cu, <0·3 per cent. A Hilger simple condensed spark unit and a Hilger medium quartz spectrograph (E 498) were used. The pin samples were machined to 3 mm diam. with the ends faced off flat, and were sparked as self electrodes. For the disc samples, the most homogeneous areas were selected, and 6-mm diam. high-purity graphite rod, machined to a sharp point, was used as counter electrode. The average reproducibilities from a series of tests, for a number of alloy samples, are tabulated; the most erratic results occurred with Al and Zn. The main conclusions reached were: (*i*) the use of cast pencils for accurate control of Al is impractical; (*ii*) extruded rod of small diam. does not appear to be a suitable alternative; (*iii*) the horizontally cast disc form probably offers the best alternative and merits further investigation.

G. C. JONES

940. **Simultaneous determination of calcium and magnesium by flame spectrophotometry.** Shigeru Yokosuka, Masao Tanaka and Humiki Morikawa (Sumitomo Metal Mine Co., Niihama, Ehime-ken, Japan). *Japan Analyst*, 1955, **4** (7), 437–440.—When a mixed soln. of Ca and Mg in 0·8 *N* HCl is submitted to flame photometry, the intensity of the line Ca 5540 A is proportional to its concn. within the range 50 to 500 p.p.m. The intensity of Mg 3710 A is proportional to its amount in the absence of Ca; in its presence, however, the measured value is the sum of Ca and Mg. By subtracting a fraction, contributed by the Ca, from the measured value, the amount of Mg (100 to 1000 p.p.m.) is calculated. Other ions that vitiate the estimation (Al, Fe, Cu, Mn, Ni, Zn and Sn) are removed by pptn. as hydroxides or sulphides. For the analysis of Ca and Mg in rocks or bricks, the sample (0·5 g) is decomposed with aqua regia or by fusing with alkali, and the aq. extract of the cake is treated with a soln. of NH_4Cl and NH_3. Both Ca and Mg are pptd. from the filtrate with a mixture of NaOH and Na_2CO_3 as $CaCO_3$ and $Mg(OH)_2$. The ppt. are dissolved in dil. HCl (1 + 10) (130 ml), made up to 200 ml with water and submitted to flame photometry. When Cu, Ni and Mn are present, they must be removed with H_2S.

K. SAITO

941. **Determination of calcium in nickel-base alloys.** V. E. Bukhtiarov. *Zavod. Lab.*, 1955, **21** (9), 1042.—The nickel alloy (0·5 g) is attacked with 25 ml of aqua regia, the excess of HNO_3 is boiled off, 20 ml of 20 per cent. HCl solution are added, the cooled solution is mixed with 30 ml of water, and then filtered into a 500-ml calibrated flask, the residue being washed 3 or 4 times with water. Aq. NH_3 is added until a ppt. appears, which is then dissolved with a few drops of 20 per cent. HCl solution; the liquid is treated with 25 ml of 10 per cent. ammonium benzoate solution and heated to boiling point. In the presence of large amounts of Cr, boiling is continued for 10 min. Sodium diethyldithiocarbamate solution (10 per cent.) (50 ml) is added to the cold solution, the vol. is made up to the mark and the solution is filtered. The filtrate (100 ml) is mixed with 30 ml of a buffer solution (20 g of NH_4Cl and 100 ml of 20 per cent. aq. NH_3 in 1 litre), 5 ml of sodium diethyldithiocarbamate solution, 10 ml of aq. NH_3 (concn. not stated), 5 drops of 0·02 *M* $K_2Cr_2O_7$ and 7 or 8 drops of Eriochrome black T solution (prepared by dissolving 0·5 g in 10 ml of buffer solution and diluting with ethanol to 100 ml). The Ca is determined by titrating with 0·01 *N* EDTA (disodium salt) solution to a green colour. Two further drops of the indicator solution are added before the end of the titration. A blank is carried out at the same time. The method has been tested over the range 0·03 to 0·5 per cent.

G. S. SMITH

942. **Estimation of calcium in alumina.** L. Jankovits and L. Erdey (Inst. Gen. Chem., Tech. Univ., Budapest). *Acta Chim. Acad. Sci. Hung.*, 1955, **7** (1–2), 155–183.—Various volumetric and colorimetric methods for the determination of Ca are investigated as to suitability for the determination of Ca in alumina. The volumetric methods include micro-titration of Ca oxalate or $K_2CaNi(NO_2)_6$ ppt. with $Ce(SO_4)_2$, and titration with EDTA (disodium salt). The colorimetric methods studied were those in which potassium nickel nitrite, picrolonic acid, naphthalhydroxamic acid and chloranilic acid were used. The most sensitive is the colorimetric method with naphthalhydroxamic acid, but it is not recommended for determining Ca in alumina because of the ppt. given by small traces of impurities. The methods recommended are the titration of $K_2CaNi(NO_2)_6$ with $Ce(SO_4)_2$, and the colorimetric estimation as calcium picrolonate and chloranilate. Analyses are conducted on the extract obtained by digesting alumina with dil. HCl (1:20) for 30 min. at 80° to 90° C. The extract is filtered off, made up to a standard vol., and an aliquot is evaporated to dryness on a water bath. The residue is taken up in warm water and the insol. matter removed by centrifuging.

J. H. WATON

943. **Paper electrophoresis. XI. Quantitative determination of small amounts of barium and aluminium by the measurement of the width of the absorption bands.** Masafumi Maki (Japan Women's Univ., Takatatoyokawa-cho, Tokyo). *Japan Analyst*, 1955, **4** (7), 413–417.—One drop of the sample soln. is spotted on a filter-paper impregnated with a buffer soln. of a const. ionic strength and submitted to paper electrophoresis (200 V) until no further migration of the band takes place. The width of the band is proportional to the amount of the ion. The specific width of the band increases with the decrease in the ionic strength of the buffer; the sensitivity of the estimation is adjusted by changing the ionic strength. Barium (150 to 1500 μg) is determined in an acetate buffer (pH 5·8), of ionic strength 0·033 to 0·05, with an error of $\pm$ 10 per cent.; aluminium (25 to 500 μg) is similarly determined in a buffer soln. (pH 2·3) of ionic strength 0·088 to 0·2. **XII. Effect of the concentration of the sample and buffer solutions on the width of bands of complex ions.** Masafumi Maki. *Ibid.*, 1955, **4** (6), 377–379.—When the cationic complex of hexa-ammino cobalt is submitted to paper electrophoresis at pH 5·7 (200 V, 110 min.), the width of the coloured absorption band is proportional to the concn. of the complex for 0·02 to 0·3 *M* soln. A similar relation holds for $Fe(CN)_6'''$ within the range 0·01 to 0·1 *M*. The width for both ions increases with the decrease in the ionic strength of the buffer soln., being nearly proportional to the reciprocal of the ionic strength.

K. SAITO

944. **New photometric determination of cadmium in copper - cadmium alloys.** W. Nielsch and G. Böltz. *Chemikerztg*, 1955, **79** (7), 364–370.—To determine 0·6 to 1 per cent. of Cd in Cu - Cd alloys, Cd is first separated as CdS; a solution of the Cd is then treated with 4-hydroxy-3-nitrophenylarsonic acid (**I**) when, at pH 3·9 to 5·9, the Cd salt is pptd. quantitatively. On dissolution in aq. NH_3 the cadmium salt is split and **I** forms a yellow colour suitable for colorimetry if interference by Cd is suppressed by EDTA (disodium salt) (**II**). *Procedure*—Dissolve the alloy (1 g) by heating in HNO_3 (1:1) (10 ml) and dilute to 100 ml. Treat 25 ml in a centrifuge tube with 20 per cent. NaOH until just turbid, then add 20 per cent. KCN (5 ml) containing 10 per cent. of Na tartrate; to the clear soln. add 20 per cent. Na_2S (5 ml), boil for 2 min., cool, and centrifuge. Wash the ppt., dissolve it in warm HNO_3 (1:1) (5 ml), and neutralise with NaOH. Add 10 per cent. acetic acid (to give a pH of 3 to 6) and then 0·35 per cent. **I** (20 ml). Boil for 1 to 2 min., centrifuge, and wash the ppt. with water (5 × 20 ml). Dissolve the ppt. in dil. (1:40) aq. NH_3 containing 0·05 per cent. w/v of **II** and make up to 250 ml. Measure the extinction and calculate the content of Cd from a calibration curve. Results on alloys containing 2·0 to 0·6 per cent. of Cd are accurate to within $\pm$ 0·5 to 2 per cent. of the amount present.

J. P. STERN

945. **Determination of mercury in ores and smelting products.** H. Dreyer and O. Lessmann (Unterharzer Berg- u. Hüttenwerke, Germany). *Erzmetall*, 1955, **8** (5), 236–240.—The determination of small amounts of Hg in sulphide ores is reviewed. The Eschka method (reduction of HgS with Fe and distillation of Hg) is too inaccurate; the dithizone method is preferred. Disperse the ore (1 g) in H_2O (10 ml) then dissolve it by boiling with conc. HCl (10 ml) and conc. HNO_3 (3 ml); after removal of nitrogen oxides, dilute the solution to 1000 ml. Add urea (10 g) to a 50-ml aliquot and extract the Hg into dithizone - CCl_4. Wash the org. phase with 0·5 *N* HCl (to remove Ag) and H_2O (20 ml) and extract Hg into 1 *N* H_2SO_4 (15 ml) containing 0·1 *N* $KMnO_4$ (1 ml). Reduce the aq. phase with a few drops of 20 per cent. hydroxylamine hydrochloride and then titrate directly with dithizone - CCl_4. Good reproducibility is obtained with 0·03 to 0·3 per cent. of Hg. For very small amounts of Hg, a distillation method followed by titration with dithizone - CCl_4 is used.

J. P. STERN

946. **Spectrochemical determination of boron in carbon and graphite.** C. Feldman and J. Y. Ellenburg (Oak Ridge National Lab., Tenn., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1714–1721.—In the d.c. arc method, from 0·5 to 4 p.p.m. of boron in carbon or graphite can be determined spectrographically by sparking 10 mg of a mixture of the sample with finely powdered Ir (as internal standard) placed in a hole in the lower of the two vertical carbon electrodes (operated at $\simeq$9 amp.). By burning the discharge in a mixture (3 + 1, by vol.) of argon and oxygen, the line pair B 2497·73 - Ir 2543·97 gives intensity ratios having a relative standard deviation of $>$ 1·8 per cent. A modified Owen fused-quartz arc chamber and an external illumination system for the grating spectrograph are used. By using a high-voltage powder-spark method the sensitivity can be extended to 0·25 p.p.m. of boron. A porous cup with a perforated floor ("sifter" electrode) is filled with $\simeq$600 mg of a mixture of the powdered sample and ignited CuO (as internal standard), forming the upper electrode, the top of which is closed with a small cork. During sparking at $\simeq 2 \times 10^4$ V, the sample is sifted into the discharge area for excitation in an atm. of argon or air. The line pair B 2497·73 - Cu 2492·15 gives a relative standard deviation of $>$ $\pm$ 1·8 per cent.; a correction is applied for interference by $>$500 p.p.m. of iron. Both methods are described in full; the arc method is preferred for small and fluffy or tacky samples, the spark method for max. sensitivity or where no argon is available, but each is supplementary.

W. J. BAKER

947. **Determination of aluminium [in zinc alloys for die-casting] by flame photometry.** Jiro Kashima and Mototaka Mutaguchi (Waseda Univ., Waseda, Tokyo). *Japan Analyst*, 1955, **4** (7), 420–423.—The intensity of the lines of Ca (422·7, 554 and 622 mμ) (and apparently those of Sr and Ba) notably decreases in the presence of Al. When Al (100 to 200 p.p.m.) is added to an aq. soln. of Ca (200 p.p.m.) and submitted to flame photometry, the intensity of the line at 422·7 mμ is reciprocally proportional to the concn. of Al. The presence of Zn in amounts $<$ 5000 p.p.m. does not affect the intensity. For the rapid analysis of Al in zinc alloys for die-casting, the sample (0·4 g) is dissolved in dil. HCl (1 + 1, 10 ml) and made up to 100 ml with $CaCl_2$ soln. to produce a soln. containing $\simeq$200 p.p.m. of Al. The product is submitted to flame photometry. The average deviation from the result of chemical analysis is less than 3 per cent. for $\simeq$4 per cent. of Al in Zn.

K. SAITO

948. **Complexiметric determination of aluminium in silicates and slags.** Yu. A. Chernikhov, B. M. Dobkina and L. M. Khersonskaya. *Zavod. Lab.*, 1955, **21** (6), 638–642.—To determine Al in silicates, 0·1 to 0·2 g is mixed with 3·5 to 5 g of NaOH and

0·5 g of Na_2O_2 in a nickel crucible, which is heated gently to fuse the NaOH and then placed in a muffle-furnace at 600° to 700° C for 15 to 20 min. The melt is extracted with 100 ml of 3·5 per cent. NaOH solution, and the solution is mixed with 0·2 to 0·6 ml (according to the concn. of Fe and Mn) of 5 per cent. sodium sulphide solution. After a few min. the solution is filtered into a 250-ml calibrated flask and the ppt. is washed 6 or 7 times with 3·5 per cent. NaOH solution. The solution is made up to the mark and an aliquot portion containing about 6 to 8 mg of Al_2O_3 diluted to 100 ml with water is mixed with 5 to 10 ml of 0·05 *M* EDTA (disodium salt) (**I**), so that the excess is $\lt$ 2 to 3 ml and $\lt$ 50 per cent. of the amount introduced. The solution is neutralised to Congo red with HCl, and 5 ml of 2 *M* chloroacetic acid, 10 ml of *M* sodium acetate and 1·5 ml of 0·1 per cent. alizarin red S solution are added. The excess of **I** is titrated with 0·05 *M* thorium nitrate solution from a micro-burette. The thorium nitrate is standardised against the **I** under the same conditions and the **I** is standardised against 0·1 *N* $CaCl_2$. One ml of 0·05 *M* **I** $\equiv$ 2·572 mg of Al_2O_3. When Ti is present its interference can be prevented by including 15 to 20 mg of CaO in the fusion mixture; only insignificant amounts of Ti then go into solution. Up to 50 mg of SiO_2 do not interfere. G. S. SMITH

949. **Photocolorimetric determination of aluminium oxide in materials of the cement industry.** I. V. Bogdanova. *Zavod. Lab.*, 1955, **21** (9), 1043.—The method is based on the use of aluminon, but preliminary separation of Fe is avoided by reducing it with ascorbic acid. The solution of the material in 0·1 *N* HCl, obtained by direct dissolution or after fusion with Na_2CO_3, etc., is treated with 1 ml of *N* HCl, 1 ml of 0·5 per cent. ascorbic acid solution (the mixture with glucose can be used) and 5 ml of 0·1 per cent. aluminon solution. The solution is made up to 50 ml in a calibrated flask with a buffer solution prepared by dissolving 27·2 g of sodium acetate in 100 to 150 ml of water, adding 10·3 ml of conc. HCl and diluting to 1 litre. The colour intensity is measured after 20 min., with a green colour filter, and the content of Al_2O_3 is read from a calibration graph. The method has been tested on various materials with contents of Al_2O_3 of 3 to 8 per cent. G. S. SMITH

950. **The spectrographic characterisation of aluminium alloys.** H. M. Hyman and S. Weisberger (Picatinny Arsenal, Dover, N.J., U.S.A.). *Applied Spectroscopy*, 1955, **9** (2), 98–101.—A general method is given for the spectrographic analysis of aluminium alloys which may be in any form or metallurgical condition. Samples, which may be as small as 0·5 g, are converted into sulphate and excited in a high-voltage a.c. graphite arc. Accuracies of 11 to 14 per cent. of content are obtained for the following elements—Mn (0·01 to 0·8 per cent.), Fe (0·1 to 6·0), Mg (0·1 to 2·0), Cu (0·3 to 10·0), Zn (0·03 to 5·0), Si (0·1 to 6·0), Cr (0·02 to 0·4), Ni (0·02 to 0·6), Ti (0·01 to 0·1), Pb (0·1 to 1·0), Ca (0·1 to 2·0 per cent.). The method is suitable for the identification of alloy types and for approx. checking to specification. P. T. BEALE

951. **Phase analysis of aluminium-base alloys.** N. I. Blok, O. A. Dubovikova-Khromova and N. F. Lashko. *Zavod. Lab.*, 1955, **21** (8), 894–899.—In the usual electrolytic method for separating phases in aluminium alloys with aqueous electrolytes the phase $CuAl_2$ is destroyed. A new method, based on the use of non-aqueous electrolytes, 2 g of LiCl in 1200 ml of methanol, 2 g of KSCN and 6 g of citric acid in 1200 ml of methanol, 2 g of ammonium acetate in 1200 ml of methanol, etc., is described. A membrane of cellulose acetate is used. To prevent ageing, the alloy with 4·85 per cent. Cu is rapidly cooled from 540° C, first in ice and salt and then in acetone. During electrolysis small portions of liquid N are introduced from time to time to maintain the surface of the sample below −7° C. G. S. SMITH

952. **A note on the control of light emission in the spectrographic analysis of aluminium alloys.** E. C. Mills and S. E. Hermon (High Duty Alloys, Ltd., Slough, England). *Metallurgia*, 1955, **52**, 212.—The control of the total amount of light emitted from the discharge, as a possible means of controlling the reproducibility of spectrographic analysis of aluminium alloys, has been investigated and the results are reported briefly. A simple unit for light control was constructed, incorporating a Mullard 90 AV vacuum photocell, and light from the analytical gap was focused on to it by a quartz lens. The output from the photocell was allowed to charge a selected condenser which, when charged, operated an electronic relay connected to the source unit and shutter. The reproducibility of the aluminium line densities was improved by about 50 per cent., but only by 10 to 20 per cent. for the alloying elements. G. C. JONES

953. **The determination of gallium with tetramethylenedithiocarbamic acid.** W. Geilmann, H. Bode and E. Kunkel (Chem. Inst., Univ. Mainz, Germany). *Z. anal. Chem.*, 1955, **148** (3), 161–176.—Gallium can be quant. determined by the use of its water-insoluble salt with tetramethylenedithiocarbamic acid (**I**). Small amounts ($\lt$ 0·2 mg) are determined nephelometrically, and larger amounts (0·2 to 5 mg) gravimetrically. High concn. of neutral salts affect the accuracy of the nephelometric procedure, and large amounts of Al, Fe, As, Sn, Se, Mo, etc., interfere in both methods and must be removed. *Nephelometric procedure*—To the almost neutral $GaCl_3$ soln. (5 ml) add tartaric acid (50 mg), 0·1 per cent. acacia mucilage (0·5 ml) and acetate buffer (2 ml). Adjust the pH to 3 to 4 with aq. HCl or Na_2CO_3 soln., add a 2 per cent. soln. of **I** (sodium salt) (1 ml) and dilute with H_2O to 10 ml. Measure the turbidity in a suitable colorimeter and calculate by use of a standard curve. *Gravimetric procedure*—To the $GaCl_3$ soln. add tartaric acid (25 mg per mg of Ga), adjust the pH to between 3·8 and 4·0, and add acetate buffer (3 to 5 ml). Dilute to 20 ml, heat to 65° C, and slowly add a soln. of **I** (sodium salt) (10 mg per mg of Ga), stirring well to coagulate the ppt. Cool to room temp. and filter by suction through a porcelain crucible. Dry for 1 to 2 hr. at 110° to 120° C and weigh as $(C_5H_8NS_2)_3Ga$. *Procedure for minerals, etc.*—To the sample in 5·5 *N* HCl add a slight excess of $TiCl_3$ soln. and extract four times with ether. Add H_2O (2 to 5 ml) to the combined ether extracts, distil off the ether at a low temp., add tartaric acid (10 to 50 mg), dilute until the HCl concn. is about 1 per cent. and saturate with H_2S. Warm to between 60° and 70° C, filter, and remove H_2S from the filtrate by a stream of CO_2 or N. Cool, adjust the pH to between 8 and 9 with NaOH soln., add Na diethyldithiocarbamate (40 to 50 mg) and extract with CCl_4 until no more colour is

extracted. Filter the aqueous layer through moist paper to remove the last traces of CCl_4, acidify with HCl and complete the determination nephelometrically or gravimetrically. A. R. ROGERS

954. **Co-precipitation of thallium (I) with silver chloride. Precipitation from homogeneous solution.** L. Gordon, J. I. Peterson and B. P. Burtt (Syracuse Univ., Syracuse, N.Y., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1770–1774.—Crystals of AgCl up to 0·2 mm in diameter were pptd. by slowly releasing $Ag^{\cdot}$ from the Ag - ammonia complex in the presence of Cl′ and 2-hydroxyethyl acetate (**I**). The co-pptn. of thallium with these crystals as carrier was studied at 5° to 60° C in 100 ml of a soln. containing NH_4Cl, aq. NH_3, **I**, and various initial concn. of $Tl_2(SO_4)_3$ and of Cl′; known weights of the solid phase were periodically analysed for ratios of Tl to Ag by the use of ^{204}Tl. The ratio of Tl to Ag in the crystal depends on the concn. of Tl in soln., the molar ratio being $\simeq 10^{-7}$. The distribution coeff. suggest an apparent homogeneous distribution of Tl within the crystals of AgCl.

W. J. BAKER

955. **Complexiметric titration of scandium with PAN as indicator.** Kuang Lu Cheng and T. R. Williams, jun. (Univ. Connecticut, Storrs, Connecticut, U.S.A.). *Chemist Analyst*, 1955, **44** (4), 96–98.—In the procedure described, 1-(2-pyridylazo)-2-naphthol (PAN) (**I**) is used as indicator for the titration of Sc with EDTA. Sodium hydroxide soln. is added to a sample soln., containing 3 to 10 mg of Sc, until a ppt. forms, then glacial acetic acid is added until the ppt. dissolves and the soln. has a pH of about 2·5. A measured excess of 0·01 *M* EDTA (disodium salt) and a few drops of **I** (0·01 per cent. in methanol) are introduced, and excess of EDTA is titrated with a 0·01 *M* soln. of Cu to a colour change from yellow to purplish red. The determination is accurate for as little as 4 mg of Sc. Alkaline-earth metals do not interfere; Zn, Al, Th, Pb and Cd interfere only slightly, but Cu, Ni and Co should be absent.

O. M. WHITTON

956. **Symposium on analysis of titanium and its alloys.** American Chemical Society. Abstracts of Papers, 128th Meeting A.C.S., Sept. 1955.—Fourteen papers with the titles given below are abstracted. **Some aspects of the analytical chemistry of titanium**, E. R. Scheffer. **Photometric determination of boron in titanium and its alloys**, R. C. Calkins and V. A. Stenger. **Determination of beryllium in titanium alloys**, L. C. Covington and M. J. Miles. **Determination of nickel in titanium alloys**, O. E. Baird and M. J. Miles. **Photometric determination of aluminium in titanium**, E. J. Benko and W. E. Campbell. **Comparison of methods for determining chlorides in titanium sponge**, A. R. Gahler and G. Porter. **The determination of trace elements in titanium by radioactivation analysis**, W. A. Brooksbank, G. W. Leddicotte and S. A. Reynolds. **Mass spectrometric studies of the evolution of gases from titanium at elevated temperatures**, W. J. McMahon and G. A. Consolazio. **The bromine trifluoride method for determining oxygen and nitrogen in titanium and titanium alloys**, H. J. O'Neill. **Some observations on the determination of oxygen by the bromination - carbon reduction method and hydrogen by the ignition method**, M. Codell and G. Norwitz. **The determination of hydrogen in titanium**, T. D. McKinley. **New electrochemical and spectrochemical methods applied to the analysis of titanium sponge, alloys and ores**, H. V. Malmstadt. **Spectrographic methods for the determination of elements in trace-to-alloying amounts in titanium**, W. M. Henry, E. R. Blosser and E. J. Center. **An evaluation of the X-ray spectrograph in the determination of titanium, manganese and iron in ilmenite and rutile ores**, S. H. Laning. Many of these papers will be published in various journals and will then be abstracted in this journal. N. E.

957. **Spectrographic analysis of titanium for impurities.** Sh. G. Melamed. *Zavod. Lab.*, 1955, **21** (9), 1066–1070.—Determinations of P, Pb, As, Sb, Sn, Bi, Si, Mg, Ca, Al, V, Fe, Ni, Cr, Co, Cu, Zr, Ag, Mo, Ta and Mn by means of a d.c. arc (more-volatile elements and lower contents of less-volatile elements) or a spark (less-volatile elements) are described. The material is first converted into the oxide form. Synthetic standards are obtained from TiO_2, from hydrolysis of pure $TiCl_4$, by mixing with the oxide of the element or, for P, with $Mg_2P_2O_7$ or $2TiO_2.P_2O_5$. G. S. SMITH

958. **The photometric determination of titanium in pure aluminium with sulphosalicylic acid.** E. Steuer and H. Dunkel (Vereinigten Aluminium-Werke A.-G., Lünen, Germany). *Aluminium*, 1955, **31** (5), 205–207.—Small amounts ($\simeq$0·005 per cent.) of Ti in Al can be determined colorimetrically in 40 min. with an accuracy of $\pm$ 5 per cent. by the use of sulphosalicylic acid (**I**). No interference is caused by V, Si, Mg, Ca and Zn, but Fe^{III} must be reduced to Fe^{II}, and Cu must be removed. *Diethyldithiocarbamate reagent*—Dissolve Pb acetate (0·2 g) in H_2O (20 ml), add 10 per cent. aq. Na K tartrate (10 ml), 10 per cent. aq. KCN (10 ml) and 1·25 per cent. aq. Na diethyldithiocarbamate (20 ml), and extract with $CHCl_3$ (250 ml). Wash the $CHCl_3$ layer with H_2O, filter, and dilute to 2 litres with $CHCl_3$. *Procedure*—Dissolve the sample (2 g) in HCl (1:1) (40 ml), add 3 per cent. aq. H_2O_2 (3 or 4 drops), cool and dilute to 100 ml with H_2O. To a 20-ml aliquot add 40 per cent. aq. **I** (15 ml), adjust to a pH of 3·3 to 3·5 with aq. NH_3 and add acetate buffer of pH 3·5 (20 ml) and 4 per cent. aq. thioglycollic acid (5 ml). Shake for 2 min. with diethyldithiocarbamate reagent (15 ml) and separate, then for 0·5 min. with $CHCl_3$ and separate, rejecting the $CHCl_3$ layer each time. Adjust the pH to about 2·7 with HCl, dilute with H_2O to 100 ml, filter into a 4-cm cuvette and, after 20 min., measure the extinction at 405 mμ.

A. R. ROGERS

959. **Gravimetric and titrimetric determination of titanium, zirconium and hafnium with cupferron. Application to fluoride solution.** P. J. Elving and E. C. Olson (Univ. Michigan, Ann Arbor, Mich., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1817–1820.—Amperometric titration and gravimetric procedures for the determination of Ti, Zr and Hf by pptn. with 5 per cent. cupferron in 10 per cent. v/v H_2SO_4 are described fully. The average error is $< \pm$ 0·4 per cent., whilst no, or only a minimum of, preliminary treatment is needed after dissolution of the sample (metal, alloy, compound) with HF and H_2SO_4. The soln. (5 to 10 ml) for amperometric titration should contain from 0·02 to 0·1 millimole of one or more of the three metals; the current is read at 1 to 1½ min. after each addition (0·5 ml) of cupferron at a potential of −0·84 V

vs. the S.C.E.; the addition of 1 per cent. gelatin soln. is optional because the applied potential is beyond that at which the max. of the cupferron wave occur. If the molar concn. of F′ is >5 times that of Ti, 10 times that of Hf or 30 times that of Zr, a large excess of 10 per cent. $AlCl_3$ soln. should be added to the sample soln. before dilution for titration. Phosphate and other complexing ions do not interfere; suspensions of zirconium or hafnium phosphate (as separated from other metals by pptn. from 10 per cent. H_2SO_4 - H_2O_2 soln.) can be readily titrated amperometrically about 5 to 10 min. after each addition of cupferron.

W. J. BAKER

960. **Spectrophotometric studies on complexes of the quadrivalent zirconium ion with polyhydroxyflavones. II. The systems with flavonol and myricetin.** L. Hörhammer, R. Hänsel and W. Hieber (Univ. Munich, Germany). *Z. anal. Chem.*, 1955, **148** (4), 251–259.—The reaction of zirconium perchlorate with flavonol (**I**) and myricetin (**II**) has been studied by Job's spectrophotometric method. In 2 *M* perchloric acid, Zr forms 1:1 and 1:2 complexes with both **I** and **II**. Values of the dissociation constants have been calculated. It is concluded that the *o*-hydroxyl group in **II** is involved in complex formation. A. R. ROGERS

961. **Separation of zirconium and hafnium using anion-exchange resins. I. Qualitative studies.** K. S. Rajan and J. Gupta (Nat. Chem. Lab., Poona, India). *J. Sci. Ind. Res., B, India*, 1955, **14** (9), 453–456.—The progressive removal of Hf from zirconium salts in a natural mixture of the two by the anion-exchange resin Amberlite (fine mesh) IRA-400 has been investigated. The resin was used in the chloride form, with glass columns 50 to 55 mm long. The fluoro complexes of Zr and Hf are eluted with H_2SO_4, when Hf is separated in the first fractions. A max. recovery of 90 per cent. of Hf-free zirconium has been obtained. The notable features of the method are its speed, the high yield, and the possibility of preparing Zr-free hafnium.

G. C. JONES

962. **Use of organic reagents in inorganic analysis. II. Determination of thorium with some anilic acids.** S. K. Datta (Govt. College, Darjeeling, India). *Z. anal. Chem.*, 1955, **148** (4), 267–273.—Of the seven phthalanilic acids studied, only those from *m*- and *p*-nitroanilines, *o*-anisidine and 1-naphthylamine are suitable as analytical reagents for Th. Separation from most foreign ions, including the cerite earths, can be effected, but double pptn. is needed with Ni, Co and U, and Zr cannot be separated at all. *Procedure*—Neutralise the sample to Congo red, dilute to 50 ml, warm to 60° C, add 2 per cent. NH_4Cl soln. (5 ml) and a 1 per cent. soln. of *m*-nitranilic acid in 50 per cent. aq. ethanol, in slight excess. Stir, filter, wash the ppt. first with hot water, then with 50 per cent. aq. ethanol, partially dry and ignite to the oxide.

A. R. ROGERS

963. **Rapid determination of carbon dioxide in silicate rocks.** L. Shapiro and W. W. Brannock (Agric. Res. Center, Beltsville, Md., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1796–1797.—In the procedure described, which takes only ≃5 min. per sample, the vol. of CO_2 evolved by HCl treatment is measured by using a glass tube (15 cm × 1·8 cm) to which is attached a calibrated side-arm (20 cm) with a closed end in which the CO_2 is collected over oil. The reaction takes place below the covering of oil in the main tube, 2 ml of 3 per cent. aq. $HgCl_2$ being added to the sample (1 g) to prevent liberation of hydrogen from any iron present. For samples containing ≯2 per cent. of CO_2 the results are as accurate as those obtained by the conventional "train" method. W. J. BAKER

964. **Spectrochemical analysis with a universal source unit. I. Determination of a minute content of silicon in iron and steel.** Jiro Kashima and Kazuo Yasuda (Waseda Univ., Waseda, Tokyo). *Japan Analyst*, 1955, **4** (7), 427–431.—A new type of universal source unit for spectrochemical analysis has been designed and constructed. The trigger circuit consists of a transformer to raise the voltage to 20 kV (peak) and of a discharge circuit with a variable condenser and a variable inductance. The phase is freely controlled and the circuit is adjusted so that reproducible currents of various characteristics are obtained, which are suitable for the analysis of iron and steel. Silicon (0·01 to 1 per cent.) in steel is determined with good accuracy under the following conditions: capacity, 40 μF; inductance, 200 μH; resistance, 50 ohms; voltage, 850 V; width of slit, 0·025 mm; preliminary discharge, 10 sec.; exposure, 10 to 60 sec.; line pair, Si 2881·6 - Fe 2880·6. K. SAITO

965. **Method for the quantitative estimation of the Si–H bond.** G. Fritz (Inst. Silicon Chem., Univ., Marburg, Germany). *Z. anorg. Chem.*, 1955, **280**, 134–142.—Monosilane is absorbed by $HgCl_2$ soln. according to the equation—

$$SiH_4 + 8HgCl_2 + 4H_2O = Si(OH)_4 + 4Hg_2Cl_2 + 8HCl.$$

The reaction is quant. and the SiH_4 absorbed is estimated by titrating the Hg_2Cl_2 ppt. iodimetrically. The method is also applicable to the determination of organic silicon compounds containing Si–H bonds. Details are given for the estimation of $(CH_3)_2SiH_2$ and $SiHCl_3$. In each instance the error is $<\pm 1$ per cent. J. H. WATON

966. **Volumetric determination of soluble silicates in detergents.** A. M. Lawson, L. A. Jones and O. T. Aepli (Pennsylvania Salt Mnfg Co., Wyandotte, Mich., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1810–1811.—A rapid and accurate method of determining SiO_2 and Na_2O in alkaline detergents is described. *Procedure*—Dissolve the sample (20 g) in water and make up the cool soln. to 1000 ml. Titrate 50 ml with *N* HCl to the first colour change with methyl red indicator. Add 5 g of NaF, shake well, then add 25 ml of ethanol and complete the titration to the red end-point (≃2 ml excess of *N* HCl). Add 0·5 ml of methyl red - xylene cyanol FF indicator (**I**) and titrate back with *N* NaOH to the greyish end-point. If carbonates or phosphates, or both, are present use methyl orange indicator in place of methyl red and then remove the CO_2 before continuing the titration as described above. If surfactants are present, add 2 or 3 drops of Foamex when removing the CO_2. The results are within ±0·05 per cent. of the gravimetric values for SiO_2. W. J. BAKER

967. **Tin determination in solders and babbitts.** C. Goldberg (New England Smelting Works, Inc., West Springfield, Mass., U.S.A.). *Chemist Analyst*, 1955, **44** (4), 103.—Tin in solders and babbitts can be determined by procedures based on the Kinnunen and Merikanto method (*cf. Chemist Analyst*, 1952,

41, 4). The original method is used for tin drosses and, omitting the addition of thiocyanate and iodide, for aluminium solders. For solders, sawings are dissolved in conc. HCl and 30 per cent. H_2O_2, with gentle heating. The solution is diluted with water and boiled to decompose H_2O_2, then water, conc. HCl and a reductant are added, and boiling is continued for 20 min. The cooled solution is titrated with standard iodine soln. in an atmosphere of CO_2, with starch as indicator. Tin in babbitt and pewter may be determined similarly, unless the copper content exceeds 3 per cent., when the copper must be removed by the procedure of Silberstein (*cf. Chemist Analyst*, 1930, **19**, 14).

O. M. WHITTON

968. **Spectrographic analysis of tin.** M. A. Rivkina, V. D. Pisarev, A. V. Kornilov, E. P. Kostrova, L. A. Kotel'nikova and M. P. Levchenko (New Siberia Inst. Railway Transport Engineers and New Siberia Tin Works). *Zavod. Lab.*, 1955, **21** (9), 1081–1083.—Spectrographic determinations of Pb, Cu, Bi, Fe, Sb and As in tin, with tin and tin-alloy electrodes, are described. G. S. SMITH

969. **Rapid electro-analytical method for the determination of lead as lead dioxide.** S. L. Jovanović and V. J. Vajgand (Chem. Inst., Belgrade, Yugoslavia). *Bull. Soc. Chim. Belgrade*, 1955, **20** (5), 335–342.—For the rapid electrolytic determination of Pb as PbO_2, 0·1 to 0·55 g of metal is dissolved in 20 ml of conc. HNO_3 plus 5 ml of 60 per cent. $HClO_4$, and made up to 170 ml. The soln. is electrolysed at 2·2 V and 1·3 A, at 60° C, for 30 min. The deposit is dried at 120° C. The conversion factor is 0·8614; in the presence of H_2SO_4, the factor is 0·856. The effects of 29 other ions are investigated; comparable amounts of Co, Cr, Na_2HPO_4, Mn, Hg, Bi, As, Mo and TiO_2 affect the results, but small amounts do not.

A. B. DENSHAM

970. **Arsenous oxide—a primary standard for the iodimetric estimation of lead and barium.** B. R. Sant (Hindu Univ., Benares, India). *Z. anal. Chem.*, 1955, **148** (3), 176–178.—Barium and lead can be determined quant. by pptn. as chromate and iodimetric titration of the ppt. with As_2O_3 soln. The results agree within $\simeq$0·2 per cent. with those by the usual gravimetric and thiosulphate methods. *Procedure*—For Pb, add *N* acetic acid (10 ml) and Na acetate (1 to 2 g) to the sample, heat to boiling point and add a measured excess of standard $K_2Cr_2O_7$ soln. Filter through a sintered-glass crucible, wash the ppt. free from dichromate, dissolve it in HCl (1:1) and dilute to 250 ml. Reduce a 50-ml aliquot with KI, adjust the pH to about 8 with borate buffer and titrate with 0·1 *N* As_2O_3 to a starch end-point. Barium is determined similarly by pptn. in the presence of NH_4Cl followed by iodimetric estimation with As_2O_3.

A. R. ROGERS

971. **The determination of small quantities of ammonia in gas mixtures.** Y. Kauko and S. Döger (Physic.-chem. Inst. Univ., Ankara). *Naturwissenschaften*, 1955, **42** (8), 209.—The gas containing the ammonia is drawn through a molar solution of NH_4Cl at 25° C until equilibrium is reached and the resulting pH is measured. The ammonia pressure is calculated from the formula $P_{NH_3} = pH - 11{\cdot}11$. One determination requires approximately 0·7 litre of gas and 0·4 ml of NH_4Cl solution and takes 30 minutes. The accuracy of the measurement is about $\pm$ 2·3 per cent. at $\Delta pH = \pm 0{\cdot}01$.

E. KAWERAU

972. **Nitrometric estimation of silver nitrite and strontium nitrite in admixture with the hyponitrites.** T. M. Oza, V. T. Oza and G. T. Oza (M.R. Science Inst., Gujarat Coll., Ahmedabad, India). *J. Indian Chem. Soc.*, 1955, **32** (7), 482.—An assay similar to that described for the determination of mixtures of nitrites and hyponitrites of Na and Ca (*Brit. Abstr. C*, 1951, 327) is given for mixtures of the same salts of Ag and Sr. The results show that the presence of hyponitrites does not cause interference in the nitrometric estimation of nitrites, but preliminary boiling and cooling (which does not affect the NO_2' present) is recommended.

H. B. HEATH

973. **Analysis for industry [determination of nitrates].** A. M. G. Macdonald. *Ind. Chem. Mfr*, 1955, **31**, 568–570.—Methods of determining nitrates reviewed are: reduction to NH_3, determination of HNO_3 in conc. H_2SO_4 by direct titration with $FeSO_4$, reduction with formic acid, and polarographic methods. (78 references.) S.C.I. ABSTR.

974. **Trace analysis with radioactive isotopes. Activation analysis of phosphorus in iron.** W. Herr (Max-Planck-Inst., Mainz). *Arch. Eisenhüttenw.*, 1955, **26** (9), 523–526.—The principles and advantages of activation analysis are discussed, with emphasis on the high sensitivity of the method and on the importance of the half-life of the decaying radio-isotope. By activation analysis, P can be determined in Fe activated for six weeks in a neutron flux of 10^{12} neutrons per sq. cm in a concn. of 0·002 per cent., w/w. Possible errors in the determination are discussed. J. P. STERN

975 **Cerimetric determination of hypophosphite.** M. N. Sastri and C. Kalidas (Andhra Univ., Waltair, India). *Rec. Trav. Chim. Pays-Bas*, 1955, **74** (8–9), 1045–1048.—Aliquots of 0·01 *M* KH_2PO_2 soln. are heated on a bath of boiling water with excess of 0·05 *N* $Ce(SO_4)_2$ in a total acidity of 1·5 to 2 *N* H_2SO_4, with 2 ml of 5 per cent. Ag_2SO_4 soln. in conc. H_2SO_4 as catalyst. After reaction of the hypophosphite is complete (20 min.), the excess of Ce^{++++} is titrated with ferrous ammonium sulphate soln., ferroin being used as indicator. In the absence of a catalyst the reaction with hypophosphite is not complete in 1 hr. The method is compared with the standard bromate method and results show good agreement within $\simeq$1 per cent. or less. A determination requires 30 min. The similar method of Bernhart (*Anal. Abstr.*, 1955, **2**, 903) gives lower results. E. J. H. BIRCH

976. **Ultra-violet spectrophotometric determination of bismuth by the iodide and thiourea methods.** N. M. Lisicki and D. F. Boltz (Wayne Univ., Detroit, Mich., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1722–1724.—The sensitivity of both the iodide and thiourea methods for the spectrophotometric determination of Bi can be increased about four-fold by measuring the absorption max. in the u.v. instead of in the visible region. In the iodide method the transmittance is measured at 337 mμ in 1 to 2 *N* H_2SO_4; in the thiourea method it is measured at 322 mμ in 1 to 2 *N* $HClO_4$, 1-cm quartz cells being used in each instance. The concn. of Bi should be 0·3 to 3 mg per 100 ml; the accuracy is highest between 0·6 and 6 p.p.m. of Bi in both

procedures, but the thiourea method is slightly more sensitive. W. J. BAKER

977. **Qualitative reaction for vanadium.** V. L. Zolotavin (S.M. Kirov Ural Polytech. Inst.). *Zh. Anal. Khim., SSSR*, 1955, **10** (3), 189–190.—The soln. (2 to 3 ml) to be tested for V is treated, dropwise, with aq. NH_3 soln., until a cloudiness appears, which is then dissolved by careful addition of 2 *N* HCl or H_2SO_4. The soln. is shaken with excess of zinc powder until gas evolution ceases, and filtered; 0·5 ml is mixed with 0·5 ml of saturated ammonium molybdate soln. A deep-blue colour indicates the presence of V. If the molybdate soln. produces a ppt., acid must be added. The only ions that interfere are $Ti^{\cdots}$, $U^{\cdots\cdot}$ and NO_3'.
G. S. SMITH

978. **Colorimetric ferrodipyridyl method of determining vanadium in iron ores.** A. I. Ponomarev and L. L. Ratina (A. A. Baĭkov Inst. Metall., Acad. Sci. Moscow). *Zavod. Lab.*, 1955, **21** (8), 918.—The method is based on the reaction between V^{IV} and Fe^{III} giving Fe^{II}, which can be determined colorimetrically with dipyridyl. *Procedure*—The ore (0·1 to 0·5 g) is fused with Na_2CO_3 and the melt is extracted with 50 to 70 ml of water. If the soln. is green, 3 or 4 drops of ethanol are added and the soln. is warmed to reduce and ppt. the Mn. The soln. is filtered through a paper previously washed with 5 per cent. Na_2CO_3 soln. and the residue is washed with hot 1 per cent. Na_2CO_3 soln., the residue then being rejected. With contents of V > 0·5 per cent. a second fusion with Na_2CO_3 is recommended. The filtrate is made acid to Congo red with HCl (1 + 1), the soln. is made up to 100 or 250 ml in a calibrated flask, and an aliquot portion is transferred to a cylinder and treated with HCl to give a concn. of 5 to 8 per cent. by vol. Freshly prepared 4 per cent. $NaNO_2$ soln. (5 ml) is added to reduce the V and, after 10 to 15 min., the excess of nitrite is destroyed by the addition of 1 g of urea. After 30 min., with occasional shaking, 1 ml of $FeCl_3$ soln. containing 0·1 mg of Fe and 1 or 2 ml of 0·5 per cent. dipyridyl soln. are added. The soln. is carefully neutralised by the dropwise addition of aq. NH_3. The end-point is reached when drops of aq. NH_3 no longer strengthen the pink - red colour of the iron complex or when Congo red paper changes colour. The soln. is made up to 100 ml with 2 per cent. borax or Na_2CO_3 soln. After 25 to 30 min. the colour intensity is compared with that of standards containing from 0·01 to 0·1 mg of Fe in 100 ml. G. S. SMITH

979. **A rapid colorimetric determination of vanadium in carbon [electrode] materials.** Ken Sugawara, Motoharu Tanaka and Akiya Kozawa (Nagoya Univ., Nagoya, Japan). *Bull. Chem. Soc. Japan*, 1955, **28** (7), 492–494.—*Procedure*—The pulverised sample (0·1 to 1 g) is ground with 2 g of Na_2CO_3, ashed at 650° to 750° C for about 20 min., and the residue is dissolved by boiling in H_2SO_4 for 5 min. To this soln. are added 5 mg of $Fe^{\cdots}$ and 50 ml of water, and the whole is neutralised, partly with 3 *N* NaOH and accurately with 3 *N* aq. NH_3 soln., *p*-nitrophenol being used as an indicator. The ppt. is filtered off and dissolved in 20 ml of hot H_3PO_4 soln. (1 : 3); 1 ml of a 0·5 *M* sodium tungstate soln. is then added. After standing for 5 min., the soln. is made up to 25 ml with water, and its extinction is determined at 410 mμ. For contents of V <30 μg slight modification of the method is necessary. Manganese (>1 mg) in the H_2SO_4 interferes, but may be removed with 30 per cent. H_2O_2 soln.; Ti, Zr, Bi, Sb and Sn also interfere.
G. R. WHALLEY

980. **Spectrographic method of determining impurities in vanadium pentoxide.** P. M. Polyakov and A. K. Rusanov. *Zavod. Lab.*, 1955, **21** (9), 1070–1075.—Methods of determining Al, Ba, Be, Bi, W, Ge, Fe, Co, Cd, Si, Mg, Mn, Cu, Mo, As, Ni, Nb, Sn, Pb, Sb, Ta, Ti, Zr, Zn and P in V_2O_5 are described. G. S. SMITH

981. **High-precision spectrophotometric microanalysis with application to vanadium - aluminium alloys.** M. Q. Freeland and J. S. Fritz (Inst. Atomic Research, Iowa State College, Ames, U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1737–1741.—Based on a modification of Beer's law, procedures are developed for using optically unmatched borosilicate-glass cells in high-precision spectrophotometric analyses involving a soln. of high extinction in the blank. Corrections are made for the thickness and transparency of the cells, and the optimum conditions for the accurate use of Hiskey's method (*Brit. Abstr. C*, 1950, 304) are indicated therefrom. These procedures are applied to the determination of V in V - Al alloys, with an error of 0·1 to 0·2 per cent., the standard peroxy - vanadium method being used and extinction measurements being made at 460 mμ (Telep and Boltz, *Brit. Abstr. C*, 1952, 246). The use of high-extinction blanks can in this way be extended to other routine analyses.
W. J. BAKER

982. **Polarographic determination of niobium and titanium from sulphuric acid solutions.** E. I. Krŷlov and V. S. Kolevatova (S.M. Kirov Ural Polytech. Inst.). *Zavod. Lab.*, 1955, **21** (8), 911–913.—Niobium in H_2SO_4 (≮ 30 per cent.) gives a polarographic wave with two steps. The half-wave potential for $Nb^{V} \rightarrow Nb^{III}$ is −1·055 V *vs.* the S.C.E. Titanium in H_2SO_4 (≮ 60 per cent.) gives a wave with a half-wave potential of −0·574 V: Ta does not give a wave under these conditions. To determine Ti and Nb in ores, etc., 0·5 g is decomposed in a platinum dish with H_2SO_4 and HF, the solution is evaporated to dryness, the residue is fused with 15 times its weight of $K_2S_2O_7$, and the melt is treated with 100 ml of 10 per cent. H_2SO_4 and H_2O_2. The SiO_2, is filtered off, the filtrate is treated with 60 ml of conc. H_2SO_4, and the solution is evaporated to fumes. The solution is then diluted to 70 per cent. H_2SO_4 with water, and 15 ml are taken for the polarographic determination. Gelatin is added as max. suppressor and H is passed through the solution. G. S. SMITH

983. **Photometric determination of niobium and tantalum in steel.** A. Eder (Gebr. Böhler, Kapfenberg, Austria). *Arch. Eisenhüttenw.*, 1955, **26** (8), 431–435.—A routine photometric method for determining Nb and Ta separately by means of their yellow - brown colour with pyrogallol in the presence of Na_2SO_3 and ammonium oxalate, respectively, is described. The colour is stable for several hours below 20° C, and dependent on pH, Nb showing its max. colour at pH 6·8 to 7·5 and Ta at pH 2·0 to 2·5. Tantalum does not interfere with the determination of Nb, but Nb has a slight absorption at pH 2·0 to 2·5. Titanium gives a similar colour reaction with pyrogallol, but a correction factor can be calculated from the intensity of the yellow colour it gives with H_2O_2. *Procedure*—Dissolve the steel in aqua regia, decompose the

carbides with H_2SO_4 - HNO_3, and ppt. Nb and Ta with aq. NH_3 (Mo dissolves, but Fe, Cr, etc., have to be separated by a further pptn.). Then prepare the stock solution by fusion of the ppt. with $KHSO_4$, dissolution of the melt in dil. acetic acid, and neutralisation with aq. NH_3. To determine Nb, add to 5 ml of stock solution, at 15° to 20° C, 1 per cent. aq. Na_2SO_3 (5 ml) and then solid pyrogallol (2·5 g); make up to 50 ml with H_2O and measure the extinction after 3 min. To determine Ta, add to 5 ml of stock solution, at 15° to 20° C, 1·1 *N* H_2SO_4 (5 ml) saturated with ammonium oxalate, and then solid pyrogallol (1·2 g); measure the extinction on this solution. Calculate the wt. of Nb or Ta from calibration curves. Results on 0·01 to 0·02 g of Nb_2O_5 or Ta_2O_5 are accurate to within ±3 per cent. J. P. STERN

984. **Spectrographic technique of determining certain impurities in tantalum.** L. S. Lomonosova. *Zavod. Lab.*, 1955, **21** (9), 1080–1081.—Determinations of Nb, Ti, Si, Fe, Sn and Ni in tantalum by means of a d.c. arc are described. G. S. SMITH

985. **Determination of oxygen in steel by a spectrographic method.** O. B. Fal'kova (I. V. Stalin Moscow Inst. Steel). *Zavod. Lab.*, 1955, **21** (9), 1083–1087.—A high-voltage impulse spark is passed between the sample of steel and a carbon rod in hydrogen gas at 40 cm pressure. The intensity of the oxygen line II 4641·8 A is compared with the background intensity near the line. With oxygen contents of 0·003 to 0·025 per cent. the results agree fairly closely with those obtained by a vacuum-fusion method. G. S. SMITH

986. **Continuous determination of ozone in gas mixtures by means of an ultra-violet photocolorimeter.** V. G. Fastovskiĭ and A. E. Rovinskiĭ. *Zavod. Lab.*, 1955, **21** (9), 1030–1032.—A differential photocolorimeter with a mercury lamp is described for continuous determination of ozone in gas mixtures. G. S. SMITH

987. **Spot-test reaction for detection of elementary sulphur.** F. Feigl and C. Stark (Ministerio da Agricultura, Rio de Janeiro, Brazil). *Anal. Chem.*, 1955, **27** (11), 1838.—The reaction depends on the formation of H_2S when free sulphur is heated with fused benzoin (benzoylphenylcarbinol) in a test-tube, or closed capillary tube, provided with paper or cotton wool moistened with aq. lead acetate. The limit of detection is ≃ 0·05 μg, and selenium does not interfere. The test is suitable for the detection of sulphur in admixture with organic or inorganic substances (insecticides, drugs, rubber, explosives, etc.), and also for the detection of benzoin. W. J. BAKER

988. **Complexiметric determination of sulphide.** P. Kivalo (Inst. Technology, Helsinki, Finland). *Anal. Chem.*, 1955, **27** (11), 1809.—The method is based on the stoicheiometric pptn. of Cu, but not of Zn or Cd, when alkaline aq. sulphide is added to a neutral or slightly acid soln. containing an excess of metal perchlorate. The accuracy is equal to that of the iodimetric method. *Procedure*—To 25 ml of 0·05 *M* cupric perchlorate soln. add 15 ml of acetate buffer (1 *M*), followed slowly by 10 to 40 ml of aq. Na_2S soln. (≃0·02 *M*), with frequent shaking. Filter off the CuS by using a fritted-glass funnel, wash the ppt. with hot water, add ≃5 ml of *M* aq. NH_3 to the filtrate until the blue colour is clear, dilute to ≃100 to 120 ml and then titrate with 0·05 *M* aq. EDTA (disodium salt) to a red - violet colour (murexide indicator). W. J. BAKER

989. **Determination of a dilute mixture of sulphurous and sulphuric anhydrides in a gaseous medium.** G. Pannetier and C. Meltzheim (Faculté des Sciences de Dijon, France). *Bull. Soc. Chim. France*, 1955, (10), 1186–1187.—Air containing the SO_2 and SO_3 is drawn through two identical bubblers containing exactly 250 ml of H_2O_2 (0·25 vol.) and a meter for the vol. of gas. After the passage of 10 litres, 50-ml samples are withdrawn and the fall in titre of the H_2O_2 (to $KMnO_4$) gives the amount of SO_2 and the acid content the amount of SO_3 + SO_3. The determination takes 1·5 hr., and in practice no change in the titre of the liquid in the second bubbler takes place. In a subsidiary experiment, the passage of 30 litres of air at 10 litres per hr. caused < 1 per cent. fall in the titre of 10-vol. H_2O_2. E. J. H. BIRCH

990. **The volumetric determination of sulphate ions.** L. Szekeres and E. Bakács (Univ. Agric. Sci., Budapest, Hungary). *Magyar Kém. Foly.*, 1955, **61** (10), 298–300.—When an ethanolic soln. of SO_4'' containing a slight excess of CO_3'' is titrated with $BaCl_2$ soln., $BaSO_4$ separates out slightly faster than $BaCO_3$. The disappearance of CO_3'' is shown by the colour change of phenolphthalein. Ether vapour excludes the air. *Procedure*—To the alkali sulphate (containing 0·05 g of SO_4'') in H_2O (3 to 5 ml), 0·1 *N* Na_2CO_3 is added so that the concn. of CO_3'' is equiv. to, or is in slight excess over, the concn. of SO_4''; ethanol (96 per cent.) is then added to give a 25 to 30 per cent. soln. Phenolphthalein (2 drops) and ether (10 to 20 drops) are added and the soln. is titrated with 0·1 *M* $BaCl_2$ until decolorised. The blank is determined similarly, the SO_4'' being omitted. With 0·01 *M* $BaCl_2$ and Na_2CO_3 soln., the ethanol concn. should be 30 per cent., and 2 ml of ether should be added. A. G. PETO

991. **Spectrophotometric determination of tetrathionate.** O. A. Nietzel and M. A. DeSesa (National Lead Co., Inc., Winchester, Mass., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1839–1841.—A method proposed by R. E. Robinson (unpublished) for determining low concn. of S_2O_6'' is based on the formation of an equiv. amount of SCN′ from tetrathionate (and higher polythionates) by reaction with CN′ in alkaline medium, followed by spectrophotometric determination of SCN′ with Fe^{+++}. The colour is developed in opaque cylinders to avoid its rapid decomposition. Robinson's procedure has been modified by using $Fe(NO_3)_3$ and HNO_3 instead of $FeCl_3$ and HCl so as to decrease the extinction of the reagent blanks, and by measuring the extinction at 460 mμ (0·02-mm slit) instead of at 525 mμ so as to double the sensitivity. Beer's law is valid for S_2O_6'' concn. of 0·5 to 5 mg per 100 ml. Interfering cations are removed by passing the sample initially over a cation-exchange resin (Amberlite IR-120). W. J. BAKER

992. **Detection and determination of selenium with ascorbic acid.** V. Simon and V. Grim (Karlovy Univ., Prague, Czechoslovakia). *Chem. Listy*, 1954, **48** (12), 1774–1778.—Under acid conditions, selenates and selenites are reduced by ascorbic acid to red Se. Quantitatively, Se (5 to 30 mg) can be determined by polarometric titration at −0·05 V with 0·1 *N* ascorbic acid in solutions adjusted to

pH 1 to 2 by means of dil. HCl or H_2SO_4. Noble metals interfere. Copper must be eliminated by pptn. as $Cu_2Fe(CN)_6$ and Fe masked by means of NaF. The reagent should be stabilised by the addition of 0·1 g of EDTA (disodium salt) and 4 ml of formic acid per litre. G. GLASER

993. **Colorimetric determination of chromium in bronze by means of the EDTA reaction.** V. G. Goryushina and E. Ya. Gallis. *Zavod. Lab.*, 1955, **21** (6), 642–644.—The colour obtained in the reaction of $Cr^{\cdots}$ with EDTA (disodium salt) (**I**) has a max. intensity at pH 3 to 5, it follows the Beer - Lambert law over the concn. range of 5 to 80 μg of Cr in 1 ml of solution, and is completely stable for weeks. Tartaric acid has no effect on the colour, citric acid reduces its intensity and oxalic acid completely prevents its development. To determine Cr in bronze, 0·5 g is dissolved in 25 ml of mixed acid [60 ml of HNO_3 (1 + 1) and 40 ml of H_2SO_4 (1 + 1)], the solution is evaporated to fumes of H_2SO_4, 70 to 75 ml of water are added and Cu is removed by electrolysis. The solution is diluted to 100 ml in a calibrated flask, 20 ml are treated with 2 ml of 5 per cent. **I** solution (prepared by dissolving 5 g of **I** in a small amount of aq. NH_3, diluting with water, filtering if necessary, neutralising to methyl red with HCl and making up to 100 ml with water), 4 or 5 drops of phenolphthalein indicator, aq. NH_3 to neutralise, and then 5 ml of 2 *N* acetic acid. The solution is boiled for 5 min., cooled, diluted to 50 ml in a calibrated flask, and the extinction is determined by means of a photocolorimeter. A calibration graph is prepared from standards containing 0·1 to 2·0 mg of Cr in 50 ml. The standards can also be used for visual determinations. G. S. SMITH

994. **Spectrophotometric determination of tungsten.** G. d'Amore (Ist. Chim. Gen. Univ., Messina). *Ann. Chim., Roma*, 1955, **45** (9–10), 759–766.—The metal, as tungstate, is allowed to react in (oxalic) acid medium at pH ≃ 2·5 with aq. $K_4Fe(CN)_6$, and the $[Fe(CN)_6.2WO_3]^{\cdots\cdot}$ complex formed is determined spectrophotometrically at 480 mμ. The influence of time and temp. and concn. of reagent on the colour have been studied. The max. amounts of $PO_4^{\cdots}$, $AsO_4^{\cdots}$, $CrO_4^{\cdot\cdot}$, $MoO_4^{\cdot\cdot}$ and $SiO_3^{\cdot\cdot}$ that can be tolerated without interference have been ascertained; $SO_4^{\cdot\cdot}$, Cl', NO_3' and $Al^{\cdots}$ do not interfere. L. A. O'NEILL

995. **Determination of certain impurities in tungsten by a spectrographic method.** N. M. Gegechkori. *Zavod. Lab.*, 1955, **21** (9), 1075–1079.—By using excitation conditions unfavourable to the development of the tungsten spectrum, the content of Si, Al, Ca, Fe and Mg can be determined by means of a d.c. arc with a medium-dispersion spectrograph. Concn. of 0·001 per cent. and upwards can be determined with an error of ±8 per cent. G. S. SMITH

996. **Extraction of uranium by 8-hydroxyquinoline and its derivatives.** C. L. Rulfs, A. K. De, J. Lakritz and P. J. Elving (Univ. Michigan, Ann Arbor, Mich., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1802–1804.—The extraction into 1 per cent. $CHCl_3$ of uranyl complexes with 0·2 per cent. solutions of 8-hydroxyquinoline (or its deriv.) can be best effected at pH 5·8 to 8 for uranyl oxinate, 5·4 to 7·2 for uranyl dichloro-oxinate (derived from 5:7-dichloro-8-hydroxyquinoline) and 5·6 to 7·3 for uranyl dibromo-oxinate. The extinctions of the resulting orange solutions can be best measured spectrophotometrically at 430, 420 and 420 mμ, respectively, in matched 1-cm cells. W. J. BAKER

997. **Alkaline iodine as an oxidant for uranium. IV.** G. S. Deshmukh and M. K. Joshi (Hindu Univ., Benares, India). *Bull. Chem. Soc. Japan*, 1955, **28** (7), 449–450.—The estimation of U is based on the reduction of U^{VI} to U^{IV}, followed by the re-oxidation of the U^{IV} with alkaline I, any excess of I being titrated with $Na_2S_2O_3$ or As_2O_3 soln. *Procedure*—(*a*) A UO_2SO_4 soln. is reduced in the cold with Zn - H_2SO_4 and set aside for 15 min., when the green colour of $UOSO_4$ appears; the soln. is filtered and the residue is washed with dil. H_2SO_4 and water. Any U^{III} is oxidised to U^{IV} by the passage of air through the cold soln. for 5 min. An excess of standard I soln. is then added, followed by 3 *N* NaOH soln. under an atmosphere of N until pptn. occurs; the whole is set aside for 15 to 20 min., when it is acidified and titrated with $Na_2S_2O_3$ soln., with starch as indicator. (*b*) The alkaline soln. from (*a*) is neutralised with dil. H_2SO_4, followed by the addition of a sodium tetraborate - boric acid buffer soln. to maintain the pH at a value suitable for an iodine - arsenite titration, *i.e.*, between 8 and 10; starch is used as indicator. 1 ml of 0·1 *N* $Na_2S_2O_3$ or As_2O_3 soln. ≡ 0·01191 g of U. The results of both procedures are comparable with those by the oxinate method. G. R. WHALLEY

998. **Gravimetric estimation of uranium as oxinate, with Complexone as a masking agent.** R. N. Sen Sarma and A. K. Mallik (Coll. Engng Tech., Calcutta, India). *Z. anal. Chem.*, 1955, **148** (3), 179–181.—Uranium (≃30 mg) has been estimated gravimetrically as oxinate, with EDTA (disodium salt) as masking agent, in the presence of (*a*) Th, Zr and rare earths (<100 mg each), (*b*) Th (100 mg), rare earths (30 mg) and P_2O_5 (100 mg), or (*c*) V (60 mg) in acid soln. In (*c*), the EDTA first reduces V^V to V^{IV}, which then forms a stable complex. A. R. ROGERS

999. **Determination of uranium in steel.** Isamu Tsubaki and Shigeo Hara (Osaka Ind. Tech. Res. Inst., Saida-cho, Ikeda, Japan). *Japan Analyst*, 1955, **4** (6), 357–358.—The separation of a small amount of U (0·2 to 7 per cent.) from a large amount of Fe was studied with synthetic samples. Quadrivalent U is pptd. from an HCl soln. of Fe^{II} with ammonium carbonate, together with Cr, V, W, Mo and a small amount of Fe; most of the Fe remains in the filtrate. The ppt. is dissolved in a mixture of HNO_3 and H_2SO_4 (U dissolves as U^{VI}) and the product is treated with ammonium carbonate to ppt. Fe, V and Mo. Uranium in the filtrate is reduced with zinc amalgam and titrated with standard $KMnO_4$ soln. This method of separation compares favourably with the cupferron method or the ether-extraction method. K. SAITO

1000. **Applications of differential spectrophotometry to the determination of uranium in various binary and ternary uranium-base alloys.** A. Bacon and G. W. C. Milner (Atomic Energy Research Estab., Harwell, England). A.E.R.E. C/R 1749, 1955, 19 pp.—A rapid high-precision spectrophotometric method is described for the determination of U in binary and ternary alloys with Zr, Mo, Ti and Nb. The determinations are carried out at

430 mμ, on samples that are 3·6 *M* to H_2SO_4. For Nb, the soln. is also made 0·2 *M* to oxalic acid to prevent hydrolysis. Each determination is carried out differentially, working from a series of standards, and correcting for the absorbancy of the alloying elements. When applied to alloys containing >40 per cent. of U, the results show a standard deviation of ±0·1 per cent. Strict control of acidity and temp. make the technique best suited for batch analysis. J. H. WATON

1001. **The chromatographic determination of the uranium content of Hungarian coal-ash.** J. Szonntagh, L. Farády and A. Jánosi (Univ. Chem. Ind., Veszprém, Hungary). *Magyar Kém. Foly.*, 1955, **61** (10), 312–314.—For coal-ash, containing 40 to 50 per cent. of SiO_2, the method of Burstall and Wells (*Analyst*, 1951, **76**, 388) has been used, with the following modifications. Whatman ashless paper No. 214 is cut into squares (10 mm × 10 mm); 10 g of this paper are activated with 5 per cent. HNO_3 (65 ml) by heating it to boiling in 3 min. and then boiling for a further 20 min. The pulp is washed successively, by suction, with H_2O (till free from NO_3'), 96 per cent. ethanol (90 ml), absolute ethanol (90 ml) and anhydrous ether (450 ml). The coal-ash (2 to 3 g, ignited at 900° C) is fused in a platinum crucible with eight times its wt. of Na_2CO_3 - K_2CO_3 and the residue is taken up in conc. HNO_3 and twice evaporated to dryness in a platinum dish (the use of porcelain leads to loss of uranium). The residue is then dissolved in HNO_3 (20 ml), filtered, washed with HNO_3, evaporated to dryness and taken up in several portions (10 to 20 ml each) of ether - HNO_3 (95 : 5 by vol.) and transferred to the column, which is then washed with several portions of the solvent (total, 100 ml). The uranium is determined photometrically, by diluting the soln. with an equal vol. of H_2O, distilling off the ether and concentrating the soln. to a small vol. in a platinum dish. Conc. H_2SO_4 (2 to 3 ml) is added and the soln. is heated till fumes of SO_3 appear. To the cooled soln., diluted to ≃25 ml and filtered, 10 per cent. $K_4Fe(CN)_6$ (5 ml, containing 1 per cent. of Na_2S) is added and the soln. is diluted to 50 ml. After 15 min., the extinction is measured photometrically at 5461 A, with a 10-mm cell. The compensating soln. contains Na_2S and $K_4Fe(CN)_6$. The calibration curve is prepared with uranyl nitrate. Reproducibility is within ±15 per cent. A. G. PETO

1002. **Estimation of lanthanum, iron and magnesium in uranium by flame photometry.** J. F. Possidoni de Albinati (Comisión Nac. de la Energía Atómica). *An. Asoc. Quím. Argent.*, 1955, **43** (2), 106–120.—Emission spectra are given for the three foreign elements named, and it is shown that increasing the pressure of acetylene and decreasing the pressure of oxygen increases the intensity of the emission. The effects of slit width, the photomultiplier and the selector key of the instrument used were studied. Calibration curves for La, Fe and Mg are given, together with the interference effects of Sr and Ba. L. G. L. UNSTEAD-JOSS

1003. **Determination of fluoride in the presence of phosphate.** T. R. F. W. Fennell (Royal Aircraft Estab., Farnborough, Hants, England). *Chem. & Ind.*, 1955, (44), 1404–1405.—In the method proposed by Belcher, Caldas and Clark (*Analyst*, 1952, **77**, 602) for the determination of F′ in the presence of PO_4''', in which lead chlorofluoride is pptd. in the presence of phosphate, a positive error for the content of F′ occurs and this is directly related to the amount of PO_4''' present. The method is modified by first removing the PO_4''' by pptn. with $AgNO_3$. The modified method is accurate for F′ (25 mg) in the presence of up to 25 mg of PO_4''' and for the determination of F in organic compounds containing F and P. N. E.

1004. **Removal of lead interference in fluoride analysis by cation-exchange resin.** C. Mader (Univ. Kansas, Lawrence, U.S.A.). *Chemist Analyst*, 1955, **44** (4), 86–87.—In the procedure described, the sample soln. is added to a cation-exchange resin, Amberlite IR-120, so that interfering Pb can be replaced by non-interfering Na. When equilibrium has been established, the solution is mixed with an ethanolic soln. of 5-phenylsalicylic acid, aq. $FeCl_3$ soln. and buffer (pH2), and the extinction is measured at 575 mμ.

O. M. WHITTON

1005. **Determination of chlorine or chlorine dioxide in dilute aqueous solutions containing oxidising ions.** M. I. Sherman and J. D. H. Strickland (Brit. Columbia Res. Council, Vancouver, B.C., Canada). *Anal. Chem.*, 1955, **27** (11), 1778–1779.—Very small concn. of Cl or ClO_2 in aq. soln. in the presence of many oxidising ions ($Fe^{\cdot\cdot\cdot}$, $Cu^{\cdot\cdot}$, CrO_4'', $Ce^{\cdot\cdot\cdot\cdot}$, $Sb^{\cdot\cdot\cdot\cdot\cdot}$, etc.) can be determined by extraction from an HCl soln. (≃2·5 *M*) into CCl_4 (5 to 50 ml), and then measuring the extinction of the extract spectrophotometrically at 327 mμ (Cl) or 355 mμ (ClO_2), taking precautions to prevent photo-decomposition. The extracts need not be filtered. The method is most suitable for contents of Cl from 1 to 12 mg per 5 ml (error ⩾2·5 per cent.) and for contents of ClO_2 from 0·1 to 5 mg per 1 ml of sample (error ⩾3 per cent.). The sensitivity for chlorine detection is ≃15 p.p.m. of Cl in 5 ml of CCl_4.

W. J. BAKER

1006. **Micro-determination of chloride by the diffusion technique and the chloride content of raw cotton.** H. Naylor (Brit. Cotton Ind. Res. Ass., Didsbury, Manchester) (*J. Text. Inst., Trans.*, 1955, **46** (9), T576–T583.—The Conway micro-diffusion technique for the determination of inorganic Cl′ (*Biochem. J.*, 1935, **29**, 2221) has been improved by absorbing the Cl in a Na_2HAsO_3 solution, which eliminates the error due to volatilisation of I from the absorbing solution. Maximum Cl recovery (99 per cent.) is obtained when the vol. of test solution is a minimum and when a relatively large amount of Na acetate is present. In applying the method to cotton, the cotton, mixed with Na_2CO_3, is ashed at 650° C. Analysis of 23 different cottons gave results, expressed as NaCl, ranging from 0·05 per cent. to 0·15 per cent. with a mean of 0·08 per cent., which are in general agreement with those of earlier workers. E. S. LANE

1007. **Amperometric determination of manganese in ferromanganese and molybdenum in ferromolybdenum.** N. M. Degterev. *Zavod. Lab.*, 1955, **21** (8), 917.—*Determination of Mo in ferromolybdenum*—The sample (2·5 g) is dissolved in 20 to 25 ml of HNO_3 (1 + 1), 40 ml of HCl (1 + 1) are added and the soln. is evaporated until salts begin to separate. Then 10 to 15 ml of HCl (1 + 1) and 150 to 200 ml of water are added, the soln. is filtered into a 500-ml calibrated flask, 30 per cent. NaOH soln. is added to neutralise the acid and to give an excess of 100 ml, and the soln. is cooled and

made up to the mark. After 10 to 15 min., part of the soln. is filtered from the pptd. $Fe(OH)_3$. To 20 ml of this filtrate are added 10 to 15 ml of HCl (1 + 1) and 4 to 5 g of NH_4Cl, and the soln. is diluted to a vol. of 70 to 80 ml. It is then titrated amperometrically at 0·8 V with 0·05 *M* $K_4Fe(CN)_6$ in 1-ml portions with a 4- or 5-ml addition at the end. The titre of the ferrocyanide is determined by means of a standard sample of ferromolybdenum. *Determination of manganese in ferromanganese*—The sample (1 g) is dissolved in 30 ml of HCl (1 + 1) with the addition of several drops of conc. HNO_3, the soln. is filtered from graphite into a 500-ml calibrated flask, the filtrate is nearly neutralised with 20 per cent. NaOH soln., and solid $BaCO_3$ is added to ppt. $Fe(OH)_3$. The soln. is cooled and made up to the mark and a part is filtered after 5 to 10 min. A 15-ml portion is taken and diluted to 75 ml. Amperometric titration is carried out at 1·6 V with 0·05 *M* $K_4Fe(CN)_6$ standardised against a standard sample of ferromanganese. G. S. SMITH

1008. **Potentiometric determination of manganese by oxidation of alkaline manganous solution with permanganate.** I. M. Issa and R. M. Issa (Cairo Univ., Giza, Egypt). *Chemist Analyst*, 1955, **44** (4), 99–101.—By procedure *A*, a mixture of 5 ml of 0·1 *N* $KMnO_4$ solution, 0·2 g of telluric acid and enough 5 *N* NaOH solution to make the mixture 0·5 to 1·5 *N* in NaOH was titrated with 0·04 to 0·01 *N* manganous salt solution. In procedure *B*, 1 to 7 ml of 0·01 to 0·02 *N* manganous salt solution, 5 ml of 0·05 *N* permanganate solution, 0·2 g of telluric acid, and enough 5 *N* NaOH solution to make the mixture about 1 *M* in NaOH were mixed. Excess of permanganate was slowly titrated to the quadrivalent state with 0·03 *N* thallous solution. By procedure *A*, accurate results can be obtained only if the titrations are performed in the presence of telluric acid, the manganous solutions are as dilute as 0·04 to 0·01 *N*, and the NaOH concentration is in the range 0·5 to 1·5 *N*. As little as 0·5 mg of manganese can be determined with fair accuracy by procedure *B*. O. M. WHITTON

1009. **Separate polarographic determination of manganese oxides of different valency.** V. S. Fikhtengol'ts (State Sci. Res. Inst. Hygiene of Work and Illness, Leningrad). *Zavod. Lab.*, 1955, **21** (9), 1036–1038.—To analyse a mixture of MnO, Mn_3O_4, Mn_2O_3 and MnO_2, several mg of sample are treated at 100° C for 60 min. with an acidified pyrophosphate solution (vol. not stated), prepared by mixing 100 ml of 2 *M* $K_4P_2O_7$ with 22·5 ml of dil. H_2SO_4 (1 + 1) and 250 to 300 ml of water and then making up to 500 ml with water. The MnO_2 is insol., but the other oxides dissolve. The solution is filtered. One portion of the filtrate is shaken for 10 min. with 0·1 g of PbO_2. Measurement of the polarographic wave at +0·1 V with reference to the saturated calomel electrode gives $Mn^{\cdots}$ corresponding to the total $Mn^{\cdot\cdot}$ plus $Mn^{\cdots}$. From another portion of the solution, $Mn^{\cdots}$ alone are found. The MnO_2 is determined by heating the washed ppt. with dil. H_2SO_4 (1 + 5) and 1 or 2 ml of *N* oxalic acid, evaporating the filtrate to dryness with a few drops of 20 per cent. HNO_3 solution, igniting the residue at 450° to 500° C for 30 to 60 min., dissolving in 0·1 *N* K_2SO_4 and measuring the polarographic wave. G. S. SMITH

1010. **Determination of manganese sulphides and oxides in carbon steel and their separation from manganese carbides.** N. F. Leve and A. B. Gurevich (Ukraine Institute of Metals). *Zavod. Lab.*, 1955, **21** (9), 1032–1035.—The sample of steel is heat-treated at 900° C for 30 min. and rapidly quenched in water to ensure that the carbides are in solid solution. It is then decomposed electrolytically with an anolyte of 0·1 *N* KBr containing 10 per cent. of sodium citrate and a catholyte of 10 per cent. $CuSO_4$ solution. The insol. residue is filtered off and stirred for 1 hr. at room temp. with 100 ml of 10 per cent. $(NH_4)_2SO_4$ solution. Manganese is determined in the solution after filtration and calculated to oxide. This represents the unstable manganese oxides. The insol. matter after dissolution of the MnO is boiled for 5 min. with 100 ml of dil. HCl (1 + 3), the solution is filtered and evaporated with 5 ml of conc. HNO_3 and 10 ml of conc. H_2SO_4 to remove organic matter, then cooled and diluted to 250 ml in a calibrated flask. An aliquot portion is analysed for Mn and the result calculated to sulphide. The matter insol. in HCl is fused with Na_2CO_3, the melt is dissolved in dil. HCl and the solution is analysed for Mn; the result is expressed as stable manganese oxide. G. S. SMITH

1011. **Volumetric persulphate - cobalt method of determining manganese in ores and minerals.** D. N. Finkel'shtein and I. B. Petropavlovskaya (Central Lab. Ural Geol. Dept., U.S.S.R.). *Zh. Anal. Khim., SSSR*, 1955, **10** (3), 180–183.—With ores containing small amounts (0·02 to 0·46 per cent.) of MnO, a catalyst containing 0·5 per cent. of $CoSO_4.7H_2O$ and 2 per cent. of $CuSO_4.5H_2O$ can completely replace $AgNO_3$ in the persulphate - arsenite method of determining Mn. The sample (0·5 to 1·0 g) is heated with 15 ml of aqua regia and then evaporated to fumes with 10 ml of dil. H_2SO_4 (1 + 1). The sides of the vessel are washed down with water and the contents are again evaporated to fumes. The liquid is cooled and 100 to 120 ml of water and 20 ml of mixed acid (750 ml of water, 125 ml of conc. H_2SO_4 and 125 ml of H_3PO_4, sp. gr. 1·7) are added. The soln. is heated to dissolve the salts and boiled with 10 ml of catalyst soln. and 20 ml of 25 per cent. ammonium persulphate soln. After decomp. of the excess of persulphate, the soln. is cooled and titrated with arsenite. With ores containing large amounts of Mn, a small amount of $AgNO_3$ is essential in the catalyst soln. The manganese ore (0·1 to 0·2 g) is then heated with 20 ml of phosphoric acid (sp. gr. 1·7) at 300° to 350° C, until dark particles disappear. The solution is mixed with 200 to 300 ml of water, 20 ml of the cobalt - copper catalyst soln. and 1 ml of 0·2 per cent. $AgNO_3$ soln., and 30 ml of 25 per cent. ammonium persulphate soln. are added slowly to the hot soln. The soln. is boiled for 4 or 5 min., kept hot for 10 to 12 min. to destroy the excess of persulphate, then cooled and titrated with 0·2 *M* ferrous ammonium sulphate containing 180 ml of conc. H_2SO_4 per litre, with 5 drops of 0·1 per cent. diphenylaminesulphonic acid soln. as indicator towards the end of the titration. G. S. SMITH

1012. **Use of silver periodate for the colorimetric determination of traces of manganese in industrial caustic soda.** Takuji Ito, Keiichi Hara and Yoshio Hoshino (Res. Lab. of Resources Utilisation, Tokyo Inst. Tech., Ookayama, Tokyo). *Japan Analyst*, 1955, **4** (6), 353–356.—Silver periodate quant. oxidises a small amount of manganese (10 to 100 μg) to permanganate within 5 min. in dil. H_2SO_4 (5 to 16 *N*) in the presence of a large amount of Na_2SO_4. The sample (NaOH, 20 g) is dissolved in

water and treated with H_2SO_4 (18 *N*, 65 ml) and $NaHSO_4$ (10 per cent., 1 ml) and heated until white fumes of H_2SO_4 are evolved (to expel chloride). The product is made up to 100 ml with water and heated with $AgIO_4$ (0·1 g) for a few min. The colour of MnO_4' is compared with a standard in a Nessler tube. The average deviation from the mean is <5 per cent. for 10 μg of Mn in 100 ml.

K. SAITO

1013. **Ultra-violet spectrophotometry of iron with tartaric acid.** Shigeru Yokosuka, Masao Tanaka and Humiki Morikawa (Sumitomo Metal Mining Co., Niihama, Ehime-ken, Japan). *Japan Analyst*, 1955, **4** (7), 434–436.—The extinction of an aq. soln. containing $Fe^{\cdots}$ (up to 40 p.p.m.) is proportional to its concn. in the presence of 1 per cent. tartaric acid (at 300 mμ at pH 8 to 10·9, or 350 mμ at pH 2·5 to 4·8). The soln. remains unchanged for two days when kept in the dark. This method appears to be suitable for the determination of Fe (1 to 20 per cent.) in rocks. The sample (0·5 g) is fused with Na_2CO_3, dissolved in dil. HCl and filtered. The filtrate is made up to 500 ml and a 5-ml portion is treated with *N* acetic acid (20 ml), *N* aq. NH_3 soln. (10 ml) and tartaric acid (10 per cent., 5 ml) and made up to 50 ml. The extinction is measured at 350 mμ. No interference results from other common components of rocks. K. SAITO

1014. **Determination of iron in glass by surface testing.** L. I. Ganago and N. A. Tananaev (Ural Polytech. Inst.). *Zavod. Lab.*, 1955, **21** (9), 1040–1041.—After treatment of the glass surface with HF confined in a ring of paraffin wax, the solution diluted with water is transferred to a platinum crucible and evaporated to dryness. The residue is mixed with 5 or 6 drops of water and 3 or 4 drops of dil. H_2SO_4 (1 + 3) and boiled for a few sec. The solution is transferred to a 10-ml cylinder and treated with 4 or 5 drops of 3 per cent. ammonium persulphate solution and 2 drops of dil. H_2SO_4 (1 + 3). After addition of 0·1 ml of saturated NH_4SCN solution for each ml of the solution the colour is compared with that from a standard glass treated similarly. (*Cf. Anal. Abstr.*, 1956, **3**, 1034.)

G. S. SMITH

1015. **The photometric determination of iron in pure aluminium and other non-ferrous metals with o-phenanthroline.** H. Pohl (Bundesanstalt für mech. und chem. Materialprüfung, Berlin). *Aluminium*, 1955, **31** (5), 207–210.—The method of the Chemikerausschuss der Gesellschaft Deutscher Metallhütten- und Bergleute for the determination of Fe in Al has been critically examined. The error is < 1 per cent. and varies according to the size of the sample and the content of Fe. The method is also applicable to light-metal alloys, and samples of Sn and Pb. Interference is caused by Zn, Cd and Ni; Sn may be removed as its tartrate complex; Mg does not interfere. The Zeiss Elektro-Photometer and the Netheler and Hinz Eppendorf-Photometer give equally accurate results. *Procedure*—Dissolve the sample (0·5 g) by warming in aq. HCl (d = 1·12) (10 ml), cool to 20° C and dilute to 250 ml. Filter, and to a 25-ml aliquot add 1 per cent. hydroxylamine hydrochloride soln. (2 ml) and 0·2 per cent. *o*-phenanthroline soln. (10 ml). Adjust to a pH of 3·5 to 3·7 with 50 per cent. sodium acetate soln. and dilute to 100 ml. After 5 min., measure the intensity of the red colour against a reagent blank, with a blue filter and 2-cm cuvettes. A. R. ROGERS

1016. **New photometric estimation of iron in the analysis of copper alloys. II. Procedure for the estimation of iron in copper alloys.** W. Nielsch and G. Böltz (Res. Inst., Fürst. Hohenzoll. Hüttenverwaltung, Laucherthal, Germany). *Metall*, 1954, **8** (21–22), 866–868.—Iron in copper alloys is estimated photometrically as the tartrate complex stabilised by $NaIO_4$ in the pH ranges 1·52 to 2·95 and 3·50 to 7·10. *Procedure*—Fine turnings (1 g) are dissolved in 25 ml of 50 per cent. HNO_3 soln. in a 300-ml Erlenmeyer flask. If Sn is present, 0·25 to 1 g of NaCl is added to the flask first. The soln. is made up to 100 ml, and 5-ml aliquots are taken, except for contents of Fe of 0·1 to 0·2 per cent., when 10-ml aliquots are used. For determinations in the pH range 1·5 to 3·0, a 5-ml aliquot is introduced into each of two 100-ml calibrated flasks. To the soln. to be used as a blank are added 20 ml of a $Na_4P_2O_7$ soln. (200 g dissolved in 800 ml of water, adjusted to pH 5·10 with 20 ml of $H_4P_2O_7$ and made up to 1 litre). To each soln. are added 2 ml of 1 per cent. $NaIO_4$ soln., 10 ml of tartaric acid soln. (250 g per litre) and 10 ml of buffer soln. (200 g of NH_4NO_3 and 80 g of sodium tartrate per litre). Both soln. are then made up to the mark. For determinations in the pH range 3·5 to 7·1, 5-ml aliquots are introduced into two 100-ml calibrated flasks, and 20 ml of $Na_4P_2O_7$ soln. are added to the blank soln. To each soln. are added 2 ml of 1 per cent. $NaIO_4$ soln., 25 ml of a buffer soln. containing 200 g of sodium tartrate and 20 g of $K_2B_4O_7$ per litre, and 5 ml of a second buffer soln. containing 300 g of ammonium acetate dissolved in 500 ml of water, adjusted to pH 5·1 with acetic acid and made up to 1 litre. Both soln. are made up to the mark. For both procedures, the size of the photometric cell depends on the content of Fe —5 cm for 0·2 to 0·7 per cent. of Fe, 2 cm for 0·7 to 2·0 per cent. of Fe, 1 cm for 1 to 5 per cent. of Fe and 0·5 cm for 5 to 10 per cent. of Fe. The extinction is measured against that of the blank with a mercury lamp at 366 mμ, with a S38E filter. Standard soln. of Fe and their respective blanks are prepared for each procedure in the three ranges 1 to 9·5 per cent., 0·2 to 1 per cent. and 0·1 to 0·2 per cent. of Fe and, from these, calibration curves are drawn. The results are accurate and reproducible, and it is claimed that the time for a determination should be <5 min. J. H. WATON

1017. **Potentiometric determination of iron and copper with quinquevalent tungsten.** I. M. Issa and A. M. Daess (Cairo Univ., Giza, Egypt). *Chemist Analyst*, 1955, **44** (4), 89–91.—The conditions are defined under which W^V can be successfully employed as a reductant for the determination of as little as 16 μg of Fe or Cu, alone or in admixture.

O. M. WHITTON

1018. **Determination of hydrogen in cast iron.** Yu. A. Klyachko, A. G. Atlasov and Yu. D. Labut'ev (Centr. Sci. Res. Inst. Ferrous Metallurgy). *Zavod. Lab.*, 1955, **21** (6), 651–658.—Vacuum fusion of samples of cast iron cooled by direct immersion in water yields appreciably more H and O than vacuum fusion of samples cooled in a copper vessel immersed in water. The presence of more than 0·010 to 0·015 per cent. of O indicates that water has penetrated into the sample. Cast-iron samples do not lose H when kept at ordinary temperatures. A vacuum-fusion apparatus with means for analysing the gases liberated is described.

G. S. SMITH

1019. **Determination of hydrogen in steel.** M. Šícha (Vítkovické železárny K. Gottwalda, Ostrava, Czechoslovakia). *Hutn. List.*, 1955, **10** (8), 479–483.—A simple portable apparatus for determining H in steel is described. Gases are separated from steel at 600° C, measured volumetrically, and the content of H is calculated by using an empirical factor, 0·82. Results obtained with this apparatus are compared with those from vacuum-fusion analyses and it is concluded that the optimum time for the new method is 80 to 100 min., this period minimising the errors due to mutual reaction between the H, water vapour and metal at the extraction temp. S.C.I. Abstr.

1020. **Potentio-coulometric determination of carbon in steel and carbides.** M. Šícha (Vítkovické železárny K. Gottwalda, Ostrava, Czechoslovakia). *Hutn. List.*, 1955, **10** (9), 535–542.—The C in a steel or carbide sample is converted by combustion, in a microchemical train, into CO_2, which is absorbed in $Ba(OH)_2$, followed by potentio-coulometric titration with 0·02 *N* HCl, with a platinum cathode and calomel anode. The sensitivity attained is ± 0·004 mg, but greater accuracy is attainable with a highly sensitive galvanometer. The method is suitable for routine determinations.

S.C.I. Abstr.

1021. **β-Mercaptopropionic acid as colorimetric reagent for the determination of cobalt.** E. Lyons (Univ. Florida, Gainesville, Fla., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1813.—From 2·5 to 20 p.p.m. of Co^{++} can be detected and determined quant., even in the presence of approx. equiv. concn. of Ni or Cu, by adding one drop of β-mercaptopropionic acid to the soln., followed by an excess of aq. NH_3 (to remove any coloration due to Ni or ppt. of Cu). The intensity of the deep-green coloration depends on the concn. of Co and can therefore be matched with reference standards.

W. J. Baker

1022. **Separation and determination of milli-microgram amounts of cobalt [from biological materials].** R. E. Thiers, J. F. Williams and J. H. Yoe (Univ. Virginia, Charlottesville, Va., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1725–1731.—In the procedure described for the separation of $\lesssim 2 \times 10^{-9}$ g of Co from biological material, *e.g.*, blood, the sample is dried and charred (i.r. lamp) and then ashed at 450° C for ≃18 hr. (muffle-furnace). The excess of alkali chlorides and Fe is removed by pptn., and by extraction with *iso*-propyl ether, respectively, and the Co is then fixed on an anion-exchange resin (Dowex 1-X8) from which it is eluted with 30 ml of 4 *M* HCl (after washing the column with 20 ml of 9 *M* HCl to remove alkali and alkaline-earth metals, Ni, Mn, etc.). The eluate is concentrated until the vol. of the final drop is ≃0·05 ml, and the Co (recovery >95 per cent.) is determined spectrophotometrically by a d.c. arc cathode-layer (graphite - Al_2O_3) method of excitation that is sensitive to 10^{-9} g of Co; 25 μg of Ni are used as internal standard and the intensity ratio of Co 3453·5 to Ni 3452·9 (or 3446·9) is determined. For concn. of 1 to 500 × 10^{-9} g of Co the standard deviation is ≃10 per cent. The optimum conditions for achieving the high sensitivity of the spectrochemical method are discussed.

W. J. Baker

1023. **Ultra-violet spectrophotometric determination of cobalt.** R. Lundquist, G. E. Markle and D. F. Boltz (Wayne Univ., Detroit, Mich., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1731–1733.—Increased sensitivity is obtained in both the thiocyanate and 1-nitroso-2-naphthol methods for determining cobalt spectrophotometrically if the extinction measurements are made at 312 mμ and pH 1·6 to 1·9 for the former method, and at 317 mμ and pH 4 to 5·5 for the latter method, 1-cm quartz cells being used in both instances. Beer's law is valid for concn. from 0·2 to 10 and from 0·2 to 2 p.p.m. of Co at 312 and 317 mμ, respectively. The variables are discussed and the limits of the interfering ions are listed. The ppt. of cobalt 1-nitroso-2-naphthoxide should be digested for ≃2 hr. before extracting it with $CHCl_3$ (3 × 30 ml) and making the final vol. up to 100 ml with $CHCl_3$. Since, in this method, 5 p.p.m. of Fe^{+++} produce an error of 45 per cent., these ions must be removed by a preliminary extraction with a mixture (1 + 1, by vol.) of ether and *N* HCl before pptn. of cobalt. W. J. Baker

1024. **Polarographic determination of nickel with calcium chloride as supporting electrolyte.** K. P. Privalova, Kh. Z. Avrutova and N. Ya. Khlopin (Molotov District Sanitary-Epidemic Station). *Zavod. Lab.*, 1955, **21** (6), 670–671.—Small additions of KSCN (0·05 ml of 1 *M* per 1 ml of 30 per cent. $CaCl_2$ solution) or pyridine (0·05 ml of 0·5 *M*) improve the shape of the polarographic wave of Ni in $CaCl_2$ and produce a linear relationship between the concn. and the diffusion current. The wave due to Cd is almost completely suppressed when pyridine is present. Thus Ni can be determined in the presence of Cd. G. S. Smith

1025. **Controlled potential electrolysis. VII. Electrolytic determination of nickel in the presence of zinc.** Masayoshi Ishibashi, Taichiro Fujinaga, Takashi Tatsumi and Kiyoshi Hirose (Kyoto University, Sakyo-ku, Kyoto). *Japan Analyst*, 1955, **4** (6), 365–367.—Reversible polarographic waves of Ni and Zn were studied in an ammoniacal soln. with a rotating cathode (1200 r.p.m.) coated with various metals. In *N* aq. NH_3 soln. containing 0·1 *M* $(NH_4)_2SO_4$, both Ni ($E_{\frac{1}{2}} = -0{\cdot}77$ V *vs.* the S.C.E.) and Zn (−1·08 V) give clear reduction waves when a cathode coated with Ni or Cu is used. This result was applied to the electrolytic determination of Ni. When an aq. soln. of Ni and Zn containing NH_3 and $(NH_4)_2SO_4$ is electrolysed with a constant potential of −0·95 V *vs.* the S.C.E. at 80° C, Ni is quant. deposited on the cathode free from Zn (for Ni <200 mg, 30 min.). The zinc content of the electrolyte must be <150 mg per 300 ml for a quant. separation to be achieved. K. Saito

1026. **Use of the spectrographic method for phase analysis of nickel ores.** Yu. A. Sherstkov and E. P. Fedina (Kemerovo Geological Dept.). *Zavod. Lab.*, 1955, **21** (9), 1060–1061.—The nickel ore is decomposed with aqua regia. The solution is analysed chemically for Ni, and the insol. material is analysed spectrographically for Ni with an a.c. arc after being mixed with SiO_2 and CuO in the ratio 3:3:1. The lines Ni 3050·8 and Cu 3063·4 A are read.

G. S. Smith

1027. **Spectrophotometric determination of rhodium with stannous chloride. Simultaneous determination of rhodium and platinum.** G. H. Ayres, B. L. Tuffly and J. S. Forrester (Univ. Texas, Austin, Tex., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1742–1744.—The procedure described is based on the measurement of the max. extinction at 475 mμ

of the stable pink-red colour formed by the addition of $SnCl_2$ in 2·5 *M* HCl to a soln. of $Rh^{\cdots}$ in conc. HCl and boiling gently for 10 min. After the addition of another 10 ml of $SnCl_2$ soln. (to replace any oxidised $Sn^{\cdot\cdot}$) and then diluting to 100 ml, the extinction is measured in a 1-cm quartz cell, with a matched cell for the blank. Beer's law is valid from 4 to 20 p.p.m. of Rh, and the extinctions are unaffected by wide variations in concn. of $SnCl_2$ and HCl. Interfering ions (those of Ru^{III}, Os^{IV}, Pd^{II}, Au^{III} and Cr^{VI}) are easily removed, but removal of $Pt^{\cdots\cdot}$ is unnecessary because Rh and Pt can be determined simultaneously from measurements of the extinction at 475 and 403 (or 560) mμ, respectively, additivity of extinctions being confirmed for 2 to 16 p.p.m. of each element. The error is $\simeq$1 per cent. for both Rh and Pt.

W. J. BAKER

1028. **Use of organic reagents in inorganic analysis. I. Palladium complexes of some anilic acids.** S. K. Datta (Govt. College, Darjeeling, India). *Z. anal. Chem.*, 1955, **148** (4), 259–266.—The analytical behaviour of the phthalanilic acids prepared from aniline, *o*- and *p*-toluidines, *o*-anisidine, *m*- and *p*-nitroanilines and 1-naphthylamine towards various metal ions has been studied. Most of the anilic acids give quant. pptn. of Th and Zr in acid soln., and some give specific colours with certain metals. The anilic acids from aniline, *p*-toluidine and naphthylamine can be used for the gravimetric determination of Pd in the pH range 2 to 4·5, but Fe, Th and Zr interfere, and Co, Ni and U must be separated by double pptn. *Procedure*—Heat the soln. ($\simeq M$ in Pd) of pH 3 to 4·5 to boiling point, stir in a slight excess of a 1 per cent. ethanolic soln. of the anilic acid of naphthylamine (or a 1 per cent. aq. soln. of the sodium salt), digest for 5 min. and set aside overnight. Filter through sintered glass, wash the ppt. successively with hot ethanol, water, and ethanol, and dry to constant weight at 115° to 120° C. The formula of the ppt. is

$$Pd(O{\cdot}CO{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}C_{10}H_7)_2.$$

A. R. ROGERS

1029. **Colorimetric determination of iridium with *p*-nitrosodimethylaniline.** A. D. Westland and F. E. Beamish (Univ. Toronto, Toronto, Canada). *Anal. Chem.*, 1955, **27** (11), 1776–1778.—The procedure described depends on the formation of a cherry-red coloration when micro amounts of Ir^{IV} (as chloride) are heated at 70° C for $\simeq$40 min. with an aq. ethanolic soln. (pH 7·3) of dimethyl-*p*-nitrosoaniline. The max. of the broad absorption band is measured at 530 mμ. An acid sample should be evaporated to dryness, first with NaCl and then with aqua regia. If non-volatile acids or salts are present, the iridium should be separated by hydrolytic pptn. with Ni as collector, the Ni being then removed by fixation on a cation-exchange resin. In samples from which the other platinum metals have been removed, the iridium values are accurate over the range of 1·5 to 10 p.p.m. W. J. BAKER

1030. **Spectrochemical determination of clays and shales.** G. Hartleif and H. Kornfeld (Dortmund-Hörder Hüttenunion, Germany). *Arch. Eisenhüttenw.*, 1955, **26** (6), 329–332.—Three methods of analysis for Al_2O_3, TiO_2, oxides of Fe, CaO and MgO are discussed. (1) For routine production samples from the same source, direct spectroscopy is attempted with the unknown, but almost invariant, content of SiO_2 of the sample as internal standard. The sample is diluted 1 in 15 with copper powder and pelleted; the counter-electrode is Cu. For contents of $Al_2O_3 < 40$ per cent., results are accurate to within $\pm$2·5 per cent., but at higher concn. of Al_2O_3 the calibration curve is non-linear and errors increase greatly. (2) The sample is fused with H_3BO_3 and Li_2CO_3 and then submitted to spectroscopy with SiO_2 as internal standard; again errors increase for contents of $Al_2O_3 > 40$ per cent., and this is attributed to the presence of varying amounts of extraneous minerals, such as diaspore. (3) The second method is extended to incorporate the use of Cu as external standard; this necessitates removal of water of crystallisation, and high accuracy of all weighings. The time required for four samples is 4 to 5 hr. All calibration curves, which are identical for clays and shales, are straight lines, and high reproducibility of results and good agreement with chemical analyses are achieved. J. P. STERN

1031. **Spectrographic analysis of clays for basic components.** É. E. Vaĭnshteĭn, T. F. Borovik-Romanova and V. V. Korolev (V.I. Vernadskiĭ Inst. Geochem. and Anal. Chem., Acad. Sci. USSR, Moscow). *Zh. Anal. Khim., SSSR*, 1955, **10** (3), 158–163.—A d.c. arc is used to obtain the content of SiO_2, Al_2O_3, MgO, Fe_2O_3 and CaO in clays. The powdered materials are mixed with CuO and carbon powder. Three lines of Cu are used as internal standards. Calibration graphs are obtained by the use of eight synthetic standards.

G. S. SMITH

1032. **Spectrographic determination of minor elements in dolomite and dinas.** P. A. Koka and G. A. Salomatina (Inst. Refractories and Building Materials, Acad. Sci., Kazakh SSR). *Zavod. Lab.*, 1955, **21** (9), 1061–1066.—Methods of determining Al_2O_3, TiO_2, CaO, MgO and total Fe in dolomite and dinas by means of an a.c. arc are described.

G. S. SMITH

1033. **Differential thermal analysis and its application to the study of building materials.** D. B. Honeyborne (D.S.I.R. Building Res. Sta., Watford, Herts., England). *Chem. & Ind.*, 1955, (24), 662–669.—The general principles and historical development of differential thermal analysis are discussed, with special reference to its application to building materials such as clays, limes, plasters and stone. The limitations of the method are considered. Its primary value is to enable the more time-consuming methods to be directed to the best advantage. N. E.

1034. **Determination of colouring matter in glass by surface testing.** N. A. Tananaev and L. I. Ganago (Ural Polytech. Inst.). *Zavod. Lab.*, 1955, **21** (9), 1039–1040.—The clean surface of a sample, and also that of a standard glass, are coated with paraffin wax and two drops of HF are placed in a hole in the wax. The liquid is stirred with a waxed rod for 5 min., 2 or 3 drops of water are added, and the solution is transferred by means of a capillary to a 10-ml cylinder. The waxed hole is washed out with water into the cylinder, the vol. is made up to between 1·5 and 2 ml, 3 or 4 drops of dil. H_2SO_4 (1 + 1) are added, the liquid is boiled for a few sec. to render it clear, the appropriate reagent is added to each cylinder, and water is added to one of the cylinders so that the colours match. The method is suitable for determining Co, Mn, Ni and Cu. (*Cf. Anal. Abstr.*, 1956, **3**, 1014.)

G. S. SMITH

1035. **Determination of moisture in Victorian brown coals.** G. M. Brown (Dept. of Mines, State Lab., Melbourne, Australia). *Aust. J. Appl. Sci.*, 1955, **6** (3), 365–375.—The validity of methods for determining H_2O in brown coal was studied. Thermal drying of small samples in air gives variable results. More accurate and reproducible values are obtained either by thermal drying at 105° to 130° C in oxygen-free nitrogen or by distillation with an immiscible solvent. For the former method (more suitable for routine tests on 1-g samples of powdered coal), the minimum-space nitrogen oven (British Standard 1016:1942) is recommended, whilst for the distillation method (more suitable for isolated determinations on large samples of coarse material) the apparatus of Bainbridge *et al.* (*Brit. Abstr. C*, 1949, 282) gives more accurate results than does the small Dean and Stark apparatus. A distillation of a 2-lb sample with toluene or xylene takes ≃4 hr. Both the oven and the distillation methods yield almost identical results and can be used interchangeably; in both, a temp. rise from 105° to 136° C increases the value obtained for the water content by ≃0·15 per cent. W. J. BAKER

1036. **Determination of calorific value of Victorian brown coals.** G. M. Brown (Dept. of Mines, State Lab., Melbourne, Australia). *Aust. J. Appl. Sci.*, 1955, **6** (3), 376–379.—Errors associated with the determination are discussed. Wet, "as-mined" brown coals can be burnt satisfactorily in a normal bomb calorimeter, although the calorific values so obtained do not always agree with those obtained by burning the air-dried sample. The difference depends on the coal-seam, and is probably caused by the differing degrees of oxidation of the coals during air-drying at 50° C for 16 hr. It is proposed that the air-drying stage should be eliminated.
W. J. BAKER

See also Abstracts 904, 911, 1074, 1085, 1192, 1193, 1205.

3.—ORGANIC ANALYSIS

1037. **Determination of total carbon in organic materials by a wet-dry combustion method.** W. P. Pickhardt, A. N. Oemler and J. Mitchell, jun. (E.I. du Pont de Nemours & Co., Inc., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1784–1788.—The method is essentially that of Oemler and Mitchell ("A Universal Combustion System," Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March, 1952), with modifications to deal more effectively with halogen interference. Provision is made for the analysis of aq. samples containing high-boiling, steam-distillable or volatile substances, and solids or liquids containing org. matter equivalent to 1 to 150 mg of CO_2 are taken for analysis. Carbon of the order of 0·5 mg per 100 ml of water can be determined with a precision and accuracy within 1 per cent. relative. G. P. COOK

1038. **Dumas nitrogen determination on the decimilligram scale.** W. J. Kirsten and B. W. Grunbaum (Univ. of Uppsala, Sweden). *Anal. Chem.*, 1955, **27** (11), 1806–1809.—The method is a modification of that of Kirsten (*Brit. Abstr. C*, 1953, 196), which involves volatilisation of the sample in CO_2 at high temp., and combustion, of the gases obtained, over NiO. The accuracy of the modification, which appears to be determined by the weighing accuracy, is equal to that of the ordinary procedures on the 5-mg scale, the standard deviation being ± 0·22 per cent. absolute for the analysis of 22 nitrogen-containing compounds.
G. P. COOK

1039. **Kjeldahl method for determination of combined nitrogen in organic substances.** A. E. Beet. *Sheffield Univ. Fuel Soc. J.*, 1955, **6**, 12–14.—Modifications of the process are reviewed. The semi-micro procedure, with $KMnO_4$ as oxidant (*cf. Anal. Abstr.*, 1954, **1**, 2953) has now been applied to org. micro-analyses. A. R. PEARSON

1040. **Application of the Volhard method in semi-micro quantitative organic analysis.** R. Belcher, J. E. Fildes and A. G. Macdonald (The University, Birmingham). *Chem. & Ind.*, 1955, (44), 1402–1404.—The method described by Wagner *et al.* (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 149) for the determination of halogens in org. compounds, by decomposition with Na_2O_2 in a semi-micro Parr bomb, finishes with a conventional gravimetric procedure. An attempt was made by the present authors to substitute for this procedure a volumetric one based on the Volhard method. Three procedures are recommended on the basis of the results obtained. S.C.I. ABSTR.

1041. **Flame photometry of organic phosphorus.** D. W. Brite (Gen. Electric Co., Richland, Wash., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1815–1816.—An investigation of the continuous band-spectrum of P from organophosphorus compounds in ethanol soln. showed that between the concn. of 0·01 and 0·03 *M* the average error was 0·0006 *M*; $Na^{\cdot}$ and $Ca^{\cdot\cdot}$ cause positive errors whilst N, I, S and Cl do not interfere in quantities equiv. to that of the P. A Beckman spectrophotometer, equipped with a flame-photometer attachment, hydrogen burner and photomultiplier, was used for making the measurements reported. Flame-emission measurements at 540 mμ were made on 10 representative organophosphorus compounds. The standard deviation for tributyl phosphate in paraffin was found to be ±0·88 per cent. at the 46 per cent. level and ±0·015 per cent. at the 1·7 per cent. level.
D. G. HIGGS

1042. **Experiments with the "red SH-reagent" [1-(4-chloromercuriphenylazo)-2-naphthol] in the quantitative estimation of thiol groups.** L. Rausch and S. Ritter (Hautklin. der Westfälischen Wilhelms-univ., Münster, Germany). *Klin. Wochschr.*, 1955, **33** (41–42), 1009–1010.—The method of Flesch and Kun (*Proc. Soc. Exp. Biol. Med.*, 1950, **74**, 249) for the estimation of −SH groups has been investigated. The time necessary for complete reaction between the −SH group and the dye has been shown to be dependent on the shaking time, molar concn. of the −SH group, the presence and concn. of neutral salts (NaCl, KCl), and concn. of protein precipitants (metaphosphoric or sulphosalicylic acid). Increasing concn. of these substances or shortening time of shaking lengthens the time necessary for complete pptn. It is suggested that modifications such as increased dilution of reactants, increased time of shaking and lengthened time allowed for pptn. are necessary to reduce experimental errors. H. F. W. KIRKPATRICK

1043. **Use of a monochromator in refractometry. Refractive indices and dispersions of high-molecular-weight hydrocarbons.** R. T. Davis, jun., and R. W. Schiessler (Pennsylvania State Univ., U.S.A.).

Anal. Chem., 1955, **27** (11), 1824–1827.—A monochromator coupled with a high-intensity tungsten-filament lamp is used as a source of narrow wavelength spread for measuring refractive indices at different wavelengths, and replaces the normal standard lamps used in refractometry. The refractive indices of 14 hydrocarbons of high molecular wt. are reported at 25° and 30° C for a series of seven wavelengths. The results were consistent to $\simeq \pm 0{\cdot}00005$ unit. G. P. Cook

1044. **The analysis of fluorocarbons. Use of infra-red spectrophotometry for the analysis of small samples.** P. B. Ayscough (National Research Council, Ottawa, Canada). *Canad. J. Chem.*, 1955, **33** (10), 1566–1571.—A method for the analysis of small quantities of mixtures of CF_4, C_2F_6 and CHF_3, based on measurement of the intensity of i.r. absorption bands in the region 1000 to 1500 cm^{-1}, is described. It was shown experimentally that C_2F_6 and CHF_3 obey Beer's law in this region and that for samples of 5 to 10 μmoles an accuracy of ± 5 per cent. can be attained. The relation between pressure and extinction for the main absorption bands of each gas was determined and used to calculate the composition of synthetic mixtures. These results were similar to those obtained by mass-spectrometric analysis. O. M. Whitton

1045. **Determination of the content of trichloroethane in dichloroethane.** V. S. Étlis and L. M. Artyukhina. *Zavod. Lab.*, 1955, **21** (8), 919–920.—Conditions for the splitting off of HCl from trichloroethane without affecting dichloroethane are described. Dichloroethane (5 g) containing trichloroethane is mixed with 15 ml of 0·2 *N* $Ba(OH)_2$ and 35 ml of pure methanol and heated at 30° to 40° C for 2 to 2·5 hr. under a reflux condenser fitted with a soda - asbestos tube to absorb CO_2 from the air. The condenser is then washed down with CO_2-free water and the excess of $Ba(OH)_2$ is titrated to methyl orange with 0·1 *N* HCl. A blank is carried out under the same conditions. A small correction due to slight decomposition of dichloroethane can be made. G. S. Smith

1046. **Analysis of glycerin.** L. Hartman (Dept. Sci. Ind. Res., Wellington, New Zealand). *Chem. & Ind.*, 1955, (44), 1407–1408.—The method recently adopted by the U.K. Glycerine Producers' Association is too elaborate for routine analyses. A simpler and more rapid modification is described. Any error due to buffers or colouring matter is compensated by using the investigated glycerol soln. in both sample and blank. The conditions are so chosen that no formic acid is produced from glycerol in the blank. Propane-1:2-diol is preferable to ethanediol for reducing the periodate. The method can be completed in half the time required for the standard procedure. N. E.

1047. **Some analytical reactions of malonaldehyde, their applications to its quantitative estimation, and the behaviour of periodic acid towards this compound.** P. Fleury, J. Courtois, W. C. Hammam and L. Le Dizet (Faculté de Pharmacie de Paris). *Bull. Soc. Chim. France*, 1955, (10), 1290–1293.—Some reactions of malonaldehyde are described. A crystalline product (m.p. $\simeq$220° C) is obtained with dimedone. When 1 ml of 5 per cent. phloroglucinol in ethanol and 0·5 ml of HCl ($d = 1{\cdot}17$) are added to 0·5 ml of malonaldehyde solution ($<0{\cdot}002$ *M*), a red colour develops which can be measured at 520 mμ after 0·5 hr. at room temp. The absorption is linear between 0·0004 *M* and 0·002 *M*. This colorimetric determination is not interfered with by HIO_4. E. J. H. Birch

1048. **Gas - liquid chromatography. Separation and identification of volatile materials [fatty acids].** A. T. James and A. J. P. Martin (Nat. Inst. Med. Res., London). *Chim. Anal.*, 1955, **37** (10), 321–326.—The method developed by James and Martin for the separation of volatile fatty acids is described. Methods of detection are discussed. K. A. Proctor

1049. **Determination of formic acid in presence of acetic acid.** B. R. Warner and L. Z. Raptis (Philip Morris, Inc., Richmond, Va., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1783–1784.—The method is based on the azeotropic distillation of formic acid with $CHCl_3$, the separated acid being then titrated. Recoveries were from 95 to 100 per cent. G. P. Cook

1050. **Estimation of acetate in zinc-plating baths.** T. H. Whitehead and H. W. Wright (Univ. Georgia, Athens, Ga., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1834–1835.—The acetate is separated from the plating soln. by a double-distillation procedure and is estimated colorimetrically with $La(NO_3)_3$ and iodine soln. at a pH carefully controlled by adding aq. NH_3. The working range is $\simeq 10^{-4}$ to 10^{-3} *M* acetate and the accuracy and precision are $\simeq \pm 10$ per cent., with occasional deviations of ± 15 per cent. G. P. Cook

1051. **Titrimetric assay of trichloroacetate.** W. A. Schneider, jun., and L. E. Streeter (Dow Chem. Co., Midland, Mich., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1774–1775.—A known amount of standard acid is added to the neutral sample, the soln. is refluxed (in the presence of dioxan) for at least 1 hr., and the residual acid is titrated with NaOH soln. Recoveries ranged from 95·5 to 100·1 per cent. in the presence of various contaminants which are usually present in commercial grades. G. P. Cook

1052. **Paper-chromatographic analysis of the C_{12} to C_{22} saturated and unsaturated fatty acids.** H. Wagner, L. Abisch and K. Bernhard (Univ. Basle, Switzerland). *Helv. Chim. Acta*, 1955, **38** (6), 1536–1541.—In the method described, paper-chromatographic analysis is followed by the measurement of the light absorption of the copper ferrocyanide complexes formed on the paper. Strips of paper (14·5 cm × 50 cm) impregnated with a petroleum fraction (boiling range 190° to 220° C) are used; 100 to 400-μg quantities of the fatty acid mixture in 0·25 per cent. benzene soln. are applied to the paper and developed with a 90 per cent. acetic acid soln., previously saturated with the petroleum. Separation requires 20 to 45 hr., after which the strips are dried at 80° to 100° C for 2 hr. and then treated with a Cu acetate soln. (1 litre of water containing 20 ml of saturated Cu acetate soln.) for 15 min. The strip is then washed in tap water acidified with acetic acid (10 litres of water containing 1 ml of acetic acid) to prevent the pptn. of the basic copper salt. The fatty acid complex is then prepared by immersion in a 1·5 per cent. $K_4Fe(CN)_6$ soln. The separated components are finally estimated by the measurement of the light absorption of the complexes, with a Lumetron colorimeter. Solid and liquid acids must be separated by the usual lead salt method, since

palmitic and oleic acids cannot be separated by the procedure described, owing to a similarity of their partition coefficients. The results are as satisfactory as those of other analytical methods.

G. R. WHALLEY

1053. **Infra-red analysis of commercial diethyl ethylmalonate.** W. H. Washburn and W. B. Brownell (Abbott Lab., N. Chicago, Ill., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1812–1813.—The method is based on the measurement of extinction at 11·18, 11·85 and 13·51 μ of a 70 per cent. soln. in CCl_4; these bands are characteristic of diethyl ethylmalonate (**I**), diethyl malonate (**II**) and diethyl diethylmalonate (**III**), respectively. Recoveries of **I** from synthetic soln. were $\simeq$ 100 per cent., **II** $\simeq$ 90 to 130 per cent. and **III** $\simeq$80 per cent. The method is sufficiently accurate for plant control.

G. P. COOK

1054. **Factors influencing quantitative determination of methylpentoses and ketohexoses with anthrone.** J. R. Helbert and K. D. Brown (Marquette Univ. Sch. Med., Milwaukee, Wis., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1791–1796.—A study was made of factors that influence the determination of methylpentoses and ketohexoses with anthrone. These included (*i*) selection of wavelength for measuring anthrone monosaccharide extinction, (*ii*) the effect of temp., (*iii*) the stability of the reagent soln. and the influence of their age, (*iv*) stability of the anthrone - carbohydrate colour, (*v*) influence of acid concn., (*vi*) adherence to Beer's law, (*vii*) influence of anthrone concn. and (*viii*) the source of the anthrone. By control of several of these factors, methylpentoses and ketohexoses can be determined with a precision equal to that for glucose.

G. P. COOK

1055. **Paper chromatography of amides.** H. Zahn and E. Rexroth (Chem. Inst. Univ. Heidelberg, Germany). *Z. anal. Chem.*, 1955, **148** (3), 181–186.—Amides can be detected on paper chromatograms by N-chlorination followed by application of KI and *o*-tolidine (*cf.* Zahn and Wolf, *Melliand Textilber.*, 1951, **32**, 317). The method is illustrated by reference to the separation of polymeric cyclic amides of 5-aminopentanecarboxylic acid, and of certain plastic textiles. *Procedure*—Suspend the chromatogram in chlorine gas for 5 to 10 min., then in ammonia gas for 2 to 3 sec. Rinse in a soln. of equal vol. of saturated aq. *o*-tolidine and 0·05 *N* aq. KI, and mark the positions of the blue spots (which fade on drying). For the detection of water-soluble amides, use a saturated soln. of KI in acetone instead of the *o*-tolidine - KI reagent.

A. R. ROGERS

1056. **Studies on hydroxamic acids. V. Colorimetric micro-determination of hydroxamic acids.** E. E. Vonesch and O. A. Guagnini (Fac. de Quím. y Farm., Univ. Nac. de Eva Peron). *An. Asoc. Quím. Argent.*, 1955, **43** (2), 101–105.—*Procedure*—To 0·5 to 1 ml of sample (0·2 to 2 mg of hydroxamic acid) is added 0·2 ml of a 2 per cent. H_2SO_4 soln., the mixture is sealed in a 5-ml hard-glass ampoule and heated at 135° to 140° C for 0·5 hr. The hydrolysate is then mixed with 0·5 ml of neutral 40 per cent. formaldehyde soln., 2·5 ml of ferrous ammonium sulphate soln. (1 per cent., slightly acidified) and water to 10 ml. If a turbidity develops on adding the reagents, 1 to 2 ml of ethanol may be added before making up to 10 ml. To the 10 ml of mixture are added, immediately before the colour comparison, 50 to 100 mg of $(NH_4)_2S_2O_8$, and the colour is compared with that of standard solutions. Results of three determinations are shown to be within 0·5 per cent. of the theoretical.

L. G. L. UNSTEAD-JOSS

1057. **Titrations of weak acids and bases related to nitroguanidine.** J. E. De Vries, S. Schiff and E. St. Clair Gantz (U.S. Naval Ordnance Test Station, China Lake, Calif., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1814–1815.—The acidic and basic character of nitroguanidines and related compounds was studied by titration with sodium methoxide in dimethylformamide and ethylenediamine and with perchloric acid in trifluoroacetic acid. In the basic solvents, azo violet was satisfactory as a visual indicator. The strengths of the acids could not be differentiated potentiometrically although the pK_a values ranged from 8·1 to 12·40. A platinum - platinum electrode system was used for titrations in trifluoroacetic acid and excellent titrations were obtained for nitroguanidine in this medium.

G. P. COOK

1058. **A general method for locating the spots on a paper chromatogram of tertiary alkyl phosphates, thiolophosphates and thionophosphates.** T. K. H. Otter (Chesterford Park Res. Stn., nr. Saffron Walden, Essex, England). *Nature*, 1955, **176**, 1078.—A highly sensitive, paper-chromatographic method by which <7 μg of organophosphorus compound containing S can be detected as very clear, distinct spots is reported. The compound on the paper chromatogram is easier to hydrolyse after treatment with N-bromosuccinimide (dissolved in acetone). Treatment with ammonium molybdate solution (*cf.* Hanes and Isherwood, *Nature*, 1949, **167**, 1107) gave blue spots after 10 to 20 min. exposure to ultra-violet light.

O. M. WHITTON

1059. **The use of amyl nitrite reagent for the identification of thiols.** I. T. Walker. *Industr. Parfum.*, 1955, **10**, 236–237.—The determination of thioglycollic acid in cold waving lotions, previously reported by Walker and Freeman (*Mfg Chem.*, 1955, **26**, 11), is modified by the use of amyl nitrite in place of nitrous acid. *Procedure*—To 5 ml of ethanol add 5 ml of amyl nitrite; mix thoroughly and add 5 ml of the mixture to 5 ml of the thiol-containing sample, previously adjusted by the addition of aq. NH_3 to a pH of 9·2 to 9·5. A stable red colour is produced. Care should be taken not to inhale the vapours. The nature of the reaction is discussed.

H. B. HEATH

1060. **Separation of primary and secondary thiols from tertiary thiols in liquid ammonia.** R. L. Hopkins and H. M. Smith (Bureau of Mines, Bartlesville, Okla., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1832–1833.—A method is described for the separation of primary and secondary alkane- and *cyclo*-alkane-thiols from tertiary alkanethiols in the C_6 to C_{10} range, with limited application to C_{12} compounds. The separation is based on the reaction of primary and secondary thiols with liquid NH_3 to form insoluble ammonium mercaptides, whereas the tertiary thiols either react incompletely or form soluble ammonium mercaptides. Separation efficiency ranged from 60 to 98 per cent. according to molecular wt. and structure of the carbon chain, and generally increased with increase of molecular wt.

G. P. COOK

1061. **Spot tests for detection and differentiation of dithionite and sodium formaldehydesulphoxylate (Rongalite).** F. Feigl and C. Costa Neto (Lab.

Mineral Products, Min. Agric., Rio de Janeiro, Brazil). *Chemist Analyst*, 1955, **44** (4), 91–94.—The spot tests described for the detection and differentiation of dithionite and sodium formaldehydesulphoxylate (Rongalite) (**I**) are not very sensitive but the reagents are readily available. On being heated above 125° C, **I** gives off H_2S, detected by lead acetate paper, but dry sodium dithionite (**II**) does not. Provided that **I** is absent, **II** can be detected by its reaction with aqueous formaldehyde to give **I** and sodium formaldehydebisulphite. Thus if a sample yields H_2S on pyrolysis only after treatment with formaldehyde, the initial presence of **II** is certain. O. M. WHITTON

1062. **The estimation of the ethylthio group of a sugar diethylmercaptal.** Susumu Hirase and Choji Araki (Inst. of Chem., Kyoto Tech. Univ., Matsugasaki, Kyoto, Japan). *Bull. Chem. Soc. Japan*, 1955, **28** (7), 481–483.—A method is described for the direct estimation of ethylthio groups in a sugar diethylmercaptal or its acetylated or methylated deriv., with no interference from any original sulphate groups. The procedure involves an initial acid hydrolysis, followed by distillation and subsequent iodimetric titration of the liberated ethanethiol—

$$R{\cdot}CH(SC_2H_5)_2 + H_2O = R{\cdot}CHO + 2C_2H_5SH$$
$$2C_2H_5SH + I_2 = C_2H_5{\cdot}S{\cdot}S{\cdot}C_2H_5 + 2HI.$$

Procedure—An apparatus similar to those employed for methoxyl determinations is used, and 20 and 5 ml of a 0·1 *N* KI - I soln. are placed in the receiver and sub-receiver, respectively, followed by equal vol. of ethanol. The sample (0·1 to 0·2 g) is hydrolysed in the reaction flask with 10 ml of *N* HCl, with a slow stream of CO_2 passing through the soln., the flask being heated to between 115° and 120° C during 30 min., and then maintained at this temp. for a further 2 hr. The excess of I in each receiver is titrated with 0·1 *N* $Na_2S_2O_3$ soln., without using starch as an indicator. Low results were obtained with penta-acetyl- and pentamethyl-D-galactose diethylmercaptal, but satisfactory results can be obtained by adding 2 ml of glacial acetic acid to the HCl to increase the solubility of the sample, and with heating periods of 4 hr. G. R. WHALLEY

1063. **Paper chromatography of flavianic and rubeanic acids.** K. Suchý (Karlovy Univ., Prague, Czechoslovakia). *Chem. Listy*, 1955, **49** (1), 143.—The separation of flavianic acid (**I**) and rubeanic acid (**II**) by chromatography on Whatman No. 1 filter-paper in a number of solvent systems has been studied. Optimum separation is obtained by using the system methanol - chloroform - toluene saturated with water (7:2:1), in which the R_F values of **I** and **II** at 18° ± 1° C are 0·94 and 0·78, respectively. The substances are readily detected by means of 2 per cent. aq. $CuCl_2$ or $CuSO_4$; **I** forms a yellow and **II** a black spot. G. GLASER

1064. **Acidimetric determination of phenols.** E. T. Lippmaa (Tallin Polytech. Inst., U.S.S.R.). *Zh. Anal. Khim., SSSR*, 1955, **10** (3), 169–174.—A high-frequency conductimetric titration method for determining phenols is described. The phenol is dissolved in a mixture of 450 ml of diethylamine, 350 ml of diethylformamide, 200 ml of pyridine and 1 g of thymol. The titrant is 0·3 *N* potassium methoxide prepared from 840 ml of pyridine, 60 ml of benzene, 108 ml of methanol and 13 g of K. Special apparatus is described. The end-point can also be found potentiometrically. G. S. SMITH

1065. **Coulometric determination of quinol with iodine.** I. Bajalović and K. Nikolić (Inst. Phys. Chem., Belgrade, Yugoslavia). *Bull. Soc. Chim. Belgrade*, 1955, **20** (5), 329–333.—Quinol is determined coulometrically with electrolytically generated iodine. The iodine is liberated at a platinum anode immersed in a stirred 1 per cent. soln. of KI, containing a phosphate buffer to maintain a pH of 8. The cathodic compartment, containing aq. KCl, is separated from the anolyte by an agar - KCl plug. Voltages of ≃3 V and currents of ≃15 mA are used. A. B. DENSHAM

1066. **Simultaneous determination of maleic anhydride and 1:4-naphthaquinone in crude phthalic acid by a polarographic method.** Masaya Kurata and Mitugu Kubota (Mitsubishi Chem. Ind., Yawata, Japan). *Japan Analyst*, 1955, **4** (6), 361–365.—Both maleic acid ($E_{\frac{1}{2}} = -0{\cdot}8$ V *vs.* the S.C.E.) and 1:4-naphthaquinone ($E_{\frac{1}{2}} = +0{\cdot}15$ V) can be polarographically determined in 0·05 *N* HNO_3 soln. by the use of $Pb(NO_3)_2$ as internal standard. Wave heights for both are proportional to the concn. within the range 0·01 to 0·05 mg per ml. The presence of a large amount of phthalic acid does not interfere with the polarogram. The sample is dissolved in water (6 mg per ml) and a 5-ml portion is mixed with $Pb(NO_3)_2$ soln. (0·17 mg per ml of 0·1 *N* HNO_3) (5 ml) and submitted to polarography at 30° C. The average deviation from the mean is <0·01 per cent. (absolute). The sample soln. becomes yellow with time, but no change in the polarogram was observed after 3 hr. K. SAITO

1067. **Competing rates of oxime formation. Determination of aromatic aldehydes in presence of aromatic ketones.** L. Fowler (Monsanto Chem. Co., St Louis, Mo., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1686–1688.—The method described, based on differences in rates of oxime formation, enables vanillin to be determined in the presence of acetovanillone (4-hydroxy-3-methoxyacetophenone); *p*-hydroxybenzaldehyde and syringaldehyde behave quant. like vanillin, and acetosyringone (4-hydroxy-3:5-dimethoxyacetophenone) behaves like acetovanillone. Recoveries of aldehyde from various mixtures were 93 to 101 per cent., and the standard deviation was ±0·4 per cent. G. P. COOK

1068. **Competing rates of oxime formation. Determination of vanillin in presence of acetovanillone.** L. Fowler, H. R. Kline and R. S. Mitchell (Monsanto Chem. Co., St. Louis, Mo., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1688–1690.—A volumetric method, in which oxime formation is used, is described for the determination of vanillin in crude concentrates from the oxidation of alkaline ligninsulphonates in which the major impurity is acetovanillone. By strict control of temp. and time of reaction, vanillin was determined in the presence of up to 30 per cent. of acetovanillone and of other impurities. The precision is within 0·3 per cent. and the accuracy is 0·5 per cent. Other aldehydes interfere. G. P. COOK

1069. **Micro-method of determining primary aromatic amines by potentiometric titration with sodium nitrite.** L. M. Litvenenko and A. P. Grekov (A. M. Gorki Kharkov State Univ.). *Zh. Anal. Khim., SSSR*, 1955, **10** (3), 164–168.—The method is based on the use of KBr as a catalyst. The amine (0·01 to 0·05 millimole) is dissolved in 5 to 20 ml of 2 to 10 per cent. HCl soln. With difficultly soluble amines the sample is first dissolved in

acetic or formic acid and then treated with HCl to give a concn. of 2 to 10 per cent. Sufficient KBr to give a 0·3 to 0·4 *N* soln. is then added and the soln. is titrated, during energetic stirring, with 0·01 *N* $NaNO_2$ from a micro-burette, with platinum and quinhydrone electrodes. An accuracy of ±1 per cent. is attainable. G. S. SMITH

1070. **Rapid detection of aniline vapours in air.** W. A. Riehl and K. F. Hager (Redstone Arsenal, Huntsville, Ala., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1768–1769.—The method is based on the change of colour of paper strips, impregnated with a mixture of furfuraldehyde and acetic acid, from white to pink in the presence of aniline vapour. The concn. range is ≃5 to 150 p.p.m. G. P. COOK

1071. **Separation of 2:4-dinitrophenylhydrazones by paper chromatography.** R. B. Seligman and M. D. Edmonds (Philip Morris, Inc., Richmond, Virginia, U.S.A.). *Chem. & Ind.*, 1955, (44), 1406–1407.—Sheets of Whatman No. 1 filter-paper (30 cm × 33 cm) were twice dipped (6 cm from the bottom of the shorter edge) in a 5·1 per cent. v/v olive-oil solution in CCl_4, air-dried, and spotted with 10 μg of the 2:4-dinitrophenylhydrazones. The papers were then formed into an open cylinder (9 cm inside diam.) and developed in an equilibrated glass chamber with methyl acetate - water (10:7) at room temp. by the ascending method. Air-drying produced yellow spots on a white background which, examined by u.v. radiation, appeared as dark spots. Spraying with 0·25 *N* NaOH in ethanol produced variously coloured spots depending on the nature of the parent carbonyl compounds. Whilst there was good separation of the phenylhydrazones of the lower aldehydes and ketones, there was no separation of the long-chain aliphatic derivatives. This was effected by using a descending method with *iso*propyl alcohol as ascending developer and lowering the olive-oil content of the modified filter-paper by using 2·6 or 1·3 per cent. in CCl_4. S.C.I. ABSTR.

1072. **Colorimetric determination of the quality of azoribamine.** V. M. Iosikova (All-Union Sci. Res. Vitamin Inst., Moscow). *Zh. Anal. Khim., SSSR*, 1955, **10** (3), 191.—Azoribamine [3:4-dimethyl-6(D)-ribitylaminoazobenzene], an intermediate product in the synthesis of riboflavine, is insol. in cold benzene, but benzene extracts a yellow impurity. Acetone dissolves the material completely. The quality of azoribamine is determined by photometric evaluation of the benzene and acetone extracts and the use of a pure sample in constructing a calibration curve. G. S. SMITH

1073. **Determination of furfural[dehyde] in petroleum stocks.** O. I. Milner and D. Liederman (Socony Mobil Oil Co., Inc., Paulsboro, N.J., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1822–1823.—The method is based on the reaction of furfuraldehyde with aniline in glacial acetic acid - benzene medium to give a red colour which, although unstable, can be measured by a max. intensity reading. The coefficient of variation is ≃±5 per cent. over the range ≃4 to 460 p.p.m. The method was applied to various petroleum stocks, both dark and colourless. G. P. COOK

1074. **Method of controlling acidity in ammonium sulphate plant.** K. H. Todhunter (Simon-Carves Ltd., Stockport, England). *Chem. & Ind.*, 1955, (44), 1399–1401.—A method for the routine measurement of free H_2SO_4 in concentrated $(NH_4)_2SO_4$ liquor in gas-works recovery plant is described which is based on the principle of measuring the heat of reaction with NaOH. The apparatus consists of a silvered Dewar vessel, acting as an adiabatic calorimeter, provided with inlets and outlets for reactants and products a stirrer (electrically driven) and a Nichrome - Eureka thermocouple. The reactants are maintained at a const. temp., in the range 60° to 80° C, before mixing and the temp. rise is measured after mixing 25 ml of test liquor with 50 ml of 5 *N* NaOH. Results covering 0 to 10 per cent. of H_2SO_4 are reported and show good reproducibility. S.C.I. ABSTR.

1075. **Polarometric titration of some photographic developing agents.** J. Zýka (Karlovy Univ., Prague, Czechoslovakia). *Chem. Listy*, 1954, **48** (12), 1864–1865.—A 0·1 *M* soln. of $K_2Cr_2O_7$ is a suitable reagent for the polarometric titration of quinol (**I**), *p*-phenylenediamine (**II**), catechol (**III**), *p*-aminophenol (**IV**) and *p*-methylaminophenol (**V**) in 10^{-2} to 10^{-4} *M* concentrations in 50 per cent. H_2SO_4, with a rotating platinum electrode as cathode, a S.C.E. as anode and a potential of +0·75 to +0·90 V. The oxidation of **I** is instantaneous, **II** and **III** require 1 to 2 min., **IV** and **V** 5 to 8 min. G. GLASER

1076. **Determination of the constituents in asbestos - glass - organic fibre textile materials.** G. Satlow (Dtsch. Wollforsch.-Inst., Techn. Hochschule, Aachen). *J. Text. Inst., Trans.*, 1955, **46** (9), T631–T632.—For blends consisting of asbestos, glass fibres and organic fibres (cotton, rayon, etc.), a method of double ignition, first at 500° C and then at 900° C, is examined. The loss of wt. of the individual fibres at 500° C averages 2·6 per cent. for chrysolite asbestos, 0·3 per cent. for glass fibres and 99 per cent. for organic textile materials; and at 900° C, 14·5, 0·5 and 99 per cent., respectively. Formulae are given and their reliability proved by examination of test samples. E. S. LANE

1077. **The determination of traces of mercury in paper-mill products.** D. E. Davis and K. Linke (Fairfield Lab., Australian Paper Manufacturers, Ltd., Melbourne). *Proc. Aust. Pulp Pap. Ind. Tech. Ass.*, 1954, **8**, 251–261.—By the method described for the routine determination of traces of Hg in paper-mill products, the Hg is volatilised and may be absorbed and estimated in the absorption soln. by titration with a $CHCl_3$ soln. of dithizone or, preferably, by the reversion technique of Irving, Andrew and Risdon (*J. Chem. Soc.*, 1949, 541). The errors are equivalent to 0·02 to 0·04 p.p.m. of Hg in the samples examined. O. M. WHITTON

1078. **Methods for the analysis of essential oils standardised by the A.F.NOR.** G. Arditti. *Industr. Parfum.*, 1955, **10**, 51–53.—A review is presented of recent proposals by the A.F.NOR for the physical and chemical analysis of essential oils. Comparisons are made with those of the International Standards Organisation (I.S.O.). H. B. HEATH

1079. **Improvements in the chromium trioxide oxidation method for analytical purposes. [Determination of volatile oils.]** M. Steiner and H. Kawinski (Pharmakogn. Inst., Bonn). *Naturwissenschaften*, 1955, **42** (11), 344.—The colour change from yellow to green that takes place when Cr^{VI} is

reduced to Cr^{III} allows for a spectrophotometric determination of Cr^{III}, as Cr^{III} absorbs strongly at 585 mμ, a region in which Cr^{VI} has only a faint terminal absorption. No intermediate oxidation product exists and the curve for Cr^{III} obeys the Beer - Lambert law. A brief boiling and immediate cooling of the reaction mixture avoids formation of the hydrated violet complex of Cr^{III}. The method has been used for the determination of very small quantities of volatile oils. E. KAWERAU

1080. **Determination of free phenol in polyoxyethylene phenyl ethers.** C. F. Smullin and F. P. Wetterau (Atlas Powder Co., New Castle, Del., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1836–1838.—The method is based on the u.v. absorption of phenol in alkaline soln. An alkaline soln. of the sample is extracted with $CHCl_3$ to remove the ethers and the phenol is determined by measurement at 288 mμ. The precision is within ±1 per cent. with an average accuracy within ±5 per cent. in the concn. range 0·008 to 0·8 per cent. of phenol. G. P. COOK

1081. **Titration of basic copolymers of acrylonitrile [vinyl cyanide] in non-aqueous solution.** C. A. Streuli (American Cyanamid Co., Stamford, Conn., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1827–1829.—The methods of non-aqueous titration for the determination of organic bases have been extended to the determination of these bases when copolymerised with vinyl cyanide. Amines, amine salts and quaternary ammonium salts in the polymer may be titrated with $HClO_4$ after dissolving the polymers in a mixture of nitromethane and formic acid. The relative precision is within ±4 per cent. The salts of pyridine derivatives may be determined in polymers by titration with 1:3-di-*o*-tolylguanidine. G. P. COOK

1082. **Determination of monomer in poly(methyl methacrylate).** Yuji Takayama (Mitsubishi Rayon Co., Ltd., Kyobashi, Tokyo). *Japan Analyst*, 1955, **4** (6), 367–372.—Methyl methacrylate monomer reacts with hydroxylamine hydrochloride in alkaline ethanol to produce the hydroxamic acid, which gives a purple colour on the addition of Fe^{+++}. The application of this colour reaction to the determination of the monomer (<0·05 per cent.) in poly(methyl methacrylate) was studied with reference to the behaviour of the polymer and benzoyl peroxide. The sample (≃100 mg) is dissolved in toluene (1 ml) and treated with ethanolic NaOH (2·5 per cent., 1 ml) and hydroxylamine hydrochloride (2·5 per cent. in ethanol, 1 ml) for 15 min. at 78° C. An ethanolic soln. of $Fe(ClO_4)_3$ is added to the product and the extinction is measured at 532 mμ. The working curve is a straight line for 4 to 30 mg of the monomer per 1 ml of toluene. Benzoyl peroxide (<0·1 per cent.) does not vitiate the determination; at higher contents the working curve must be calibrated by the use of pure benzoyl peroxide. For the prep. of the ferric soln., Fe (0·4 g) is dissolved in HNO_3 (1 + 3, 20 ml) and heated with 60 per cent. $HClO_4$ (20 ml) until white fumes are produced. The product is dissolved in water (30 ml) and conc. HNO_3 (10 ml) and made up to 100 ml with 60 per cent. $HClO_4$. A 1-ml portion is mixed with 100 ml of ethanol before use. K. SAITO

1083. **Determination of benzoyl peroxide in poly(methyl methacrylate). III. Spectrophotometric determination with potassium iodide.** Yuji Takayama and Kinuko Doi (Mitsubishi Rayon Co., Ltd., Kyobashi, Tokyo). *Japan Analyst*, 1955, **4** (6), 349–353.—Benzoyl peroxide (**I**) oxidises KI in methanol and gives iodine equiv. in amount to **I**. When the extinction is measured at 372 mμ, it obeys Beer's law up to 0·12 mg of **I** per 10 ml. No interference results from the presence of methyl methacrylate monomer and polymer. The sample is dissolved in $CHCl_3$ (200 mg per 7 ml), made up to 10 ml with a methanolic soln. of KI (1 per cent.) and kept at 45° C for 40 min. The extinction, which remains unchanged for 3·5 hr., is measured with a spectrophotometer at 372 mμ. The results agree well with those obtained by the polarographic method (*Anal. Abstr.*, 1956, **3**, 164). K. SAITO

1084. **Flame photometry and [absorption] spectrophotometry can play a bigger role in analytical paint control.** D. S. Cox. *Canad. Paint Varn. Mag.*, 1955, **29** (4), 10–14, 42.—The construction and operation of the Beckman photo-electric flame photometer and the advantages and limitations of flame spectrophotometry are discussed. Tables show the emission wavelengths and detection limits for 19 metals, and the results obtained for the determination of the metals in Co octoate, Pb naphthenate and Fe_2O_3, and of Mn in a varnish are compared with those obtained by normal chemical methods. Brief reference is made to the use of u.v. spectrophotometry in the colorimetric determination of metals, and its value for the identification and qualitative analysis of drying oils and alkyd resins is discussed in more detail. D. R. DUNCAN

1085. **Determination of magnesium, total phosphorus and free phosphate in rubber.** M. E. Tunnicliffe (Dunlop Research Centre, Birmingham). *I.R.I. Trans.*, 1955, **31** (5), 141–149.—Sources of error in the molybdenum blue method for Mg and P in latex are critically evaluated, and a modified procedure is developed, ensuring complete pptn. of Mg and quant. conversion of the PO_4''' into molybdenum blue (with $FeSO_4$ as preferred reducing agent). For the estimation of Mg, 5 g of dry latex film are oxidised with 10 drops of conc. HNO_3, Ca is removed by addition of 0·5 ml of Na acetate solution (50 g of hydrated salt in 100 ml of water) and 0·5 ml of saturated ammonium oxalate solution, followed by neutralisation to methyl orange with aq. NH_3 and filtration with a filter-stick after 30 to 60 min. The Mg in the filtrate is pptd. as $MgNH_4PO_4$ and the ppt. is dissolved in 50 per cent. v/v H_2SO_4, rinsing the apparatus with 10 ml of H_2O and making up to 25 ml. An aliquot containing about 0·05 mg of Mg is taken, 1 ml of ammonium molybdate solution (equal vol. of 7·5 per cent. soln. and 10 *N* H_2SO_4) and 5 ml of freshly prepared $FeSO_4$ solution (5 per cent. w/v in 1 per cent. v/v H_2SO_4) are added and the vol. is made up to 25 ml. The extinction of this solution is measured (Ilford 608 filter), and compared with that of a mixture of 1 ml of ammonium molybdate solution and 5 ml of $FeSO_4$ solution made up to 25 ml. A calibration curve must be prepared from a series of standard solutions. For the estimation of total P, 0·1 g of dried film is evaporated with 2 ml of 10 per cent. ethanolic $Mg(NO_3)_2$ in a porcelain crucible, and then heated more strongly, finally at 500° C in a muffle-furnace for 30 min. Five ml of water are added to the cold residue together with sufficient dil. H_2SO_4 to dissolve the residue on warming. Solution is effected by heating on a water bath for 3 hr. One ml of molybdate reagent

and 5 ml of $FeSO_4$ solution are added, the vol. is made up to 25 ml and the colour is estimated as for Mg. For the determination of free PO_4''', NH_3 is removed by air-blowing 0·5 to 3 g of latex, which is coagulated by dilution to 5 ml and addition of 10 per cent. trichloroacetic acid. The mass is filtered through a column (100 mm × 8 mm) of Amberlite 1R-112H resin (previously soaked in 10 per cent. aq. HCl, washed with 10 to 20 ml of 10 per cent. HCl and then with water), followed by washing with water, collecting the filtrate and making up to 25 ml after addition of 1 ml of molybdate solution and 5 ml of $FeSO_4$ solution. The colour is then estimated as in the determination of Mg.

J. L. PROSSER

1086. **Vegetable tanning. XI. Two new methods for determining the acidity of vegetable-tanned leather.** D. Burton and L. Ma (Procter Internat. Res. Lab., Leeds Univ., England). *J. Soc. Leath. Tr. Chem.*, 1955, **39** (9), 286–300.—Dry samples of leather are immersed in pure methanol for 6 to 8 hr. before extraction in a Soxhlet apparatus with 400 ml of methanol for 30 hr. For mineral acidity, the methanolic extract is evaporated to 30 ml, diluted with 100 ml of water, boiled for 1 to 2 min., cooled, and titrated with 0·1 *N* NaOH to pH 4. For organic acidity, the methanolic extract is concentrated, diluted with water, the methanol distilled off, and the aq. soln. is titrated with NaOH soln. to pH 7. Free strong acidity is determined by extracting vacuum-dried samples of leather in a soln. of sodium acetate in a mixture of ethanediol and *iso*propyl alcohol (1 : 1) for 48 hr. at room temp., and titrating the filtrate with 0·25 *N* HCl in the same solvent.

B. R. HAZEL

1087. **New method for determining phthalate esters in propellants.** J. Grodzinski (Cent. Lab., Israeli Military Ind., Min. Defence, Israel). *Anal. Chem.*, 1955, **27** (11), 1765–1767.—The method is based on the reduction of nitroesters and nitroaromatic materials with titanous chloride and extraction of the phthalate esters into light petroleum. The phthalates are determined by saponification and titration. The procedure was applied to the determination of dimethyl, diethyl, dibutyl, dipentyl and diphenyl phthalates in nitroglycerin, dinitrotoluene, diphenylamine, ethyl centralite and ethyl acetate soln. and also in smokeless powders. Recoveries ranged from 99·6 to 100·4 per cent. and precision for the powder determinations was ≃0·025 per cent. A procedure for identifying the esters is also given.

G. P. COOK

See also Abstracts 966, 987, 1003, 1006, 1172.

4.—BIOCHEMISTRY
INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Blood, Bile, Urine, etc.

1088. **Use of metaphosphoric acid in preparation of clear protein-free filtrates.** R. P. McDonald. *Amer. J. Clin. Path.*, 1955, **25** (3), 343.—The addition of 6 ml of 0·52 *N* HPO_3 to 3 ml of plasma or serum diluted with an equal vol. of CO_2-free water gives a clear protein-free filtrate essential for the spectrophotometric determination of ascorbic acid content. The reagent is prepared by dissolving ≃6 g of the acid in water and diluting to 100 ml. A 5-ml aliquot is titrated against 0·1 *N* NaOH to phenolphthalein. The normality is determined and adjusted to 0·52 *N*. The soln. should be freshly prepared.

R. S. TONKS

1089. **The spectrophotometric determination of methaemoglobin in human blood.** M. J. Handelé and W. G. Zijlstra. *Proc. Kon. Ned. Akad. Wet., C*, 1955, **58** (5), 652–658.—The method described involves the measurement of extinction at two wavelengths, with an isosbestic point, in the visible spectrum. The standard deviation of the spectrophotometric values is ±1 to 2 per cent. of methaemoglobin in the range 0 to 50 per cent.

P. HAAS

1090. **The estimation of calcium, magnesium, zinc and iron in animal tissues.** R. Hamm (Chem.-Physikal. Inst. der Bundesforsch. für Fleischwirtsch., Kulmbach, Germany). *Biochem. Z.*, 1955, **327** (2), 149–162.—The tissues are ashed, then a soln. of the dry ash in HCl is passed through a cation exchanger (Lewatit S100) which separates phosphate and 90 to 95 per cent. of the Fe from Ca, Mg and Zn. Iron is subsequently estimated by the phenanthroline method. After elution with 5 *N* HCl, the Ca, Mg and Zn are estimated by compleximetric titration with EDTA (disodium salt), murexide and Eriochrome black T being used as indicators for Ca, and Ca plus Mg, respectively; chloral hydrate is then added to give a further end-point for Zn.

G. W. CAMBRIDGE

1091. **Polarographic determination of lead in blood.** L. Mazza, E. Scotti and B. M. Bruno (Ist. Chim. Gen. Univ., Genoa). *Ann. Chim., Roma*, 1955, **45** (9–10), 797–804.—The sample of blood (10 ml) is ashed with HNO_3, followed by HCl, and the ash is dissolved in a mixture (2 : 1 by vol.) of 0·1 *N* acetic acid and aq. $NH_2OH.HCl$ (50 per cent.). The solution is heated at 90° C to reduce Fe''', and the Pb is determined polarographically after addition of gelatin and passage of a current of H. A precision of ±5 μg of Pb per 100 ml of blood is attained.

L. A. O'NEILL

1092. **Estimation of total nitrogen in biological material.** E. Zymny. *Dtsch. Apothztg*, 1955, **95** (43), 1035–1036.—Disadvantages of the Kjeldahl estimation for total N are briefly described, and the alternative method of Autenrieth and Taege, which relies on the colorimetric determination of NH_3 with Nessler reagent, is discussed. About 100 ml of the sample are vigorously heated with 5 ml of conc. H_2SO_4, 5 g of K_2SO_4 and 0·05 g of a selenium catalyst for 1 hr. in a Kjeldahl flask and, after being cooled, the soln. is washed into a 1-litre calibrated flask with ammonia-free water, and with further cooling, made alkaline with aq. 20 per cent. NaOH soln., and diluted to the mark with water. The flask is stoppered and set aside for 1 hr., when a 25-ml aliquot is removed and diluted to 100 ml with water, to which are then added 2 ml of Nessler reagent; after 2 min. the colour is determined, and the content of N is calculated by comparison with standard curves.

G. R. WHALLEY

1093. **Comparative study of colorimetric determinations of phosphorus. Search for a highly sensitive method suitable for the determination of organic phosphorus in spots after chromatography.** J.-L. Delsal and H. Manhouri (Inst. d'Etat des Serums, Hessarek, Iran). *Bull. Soc. Chim. Biol.*, 1955, **37** (9–10), 1041–1053.—A critical review of the sensitivity of various methods has led to the following

conclusions. If the spectrophotometer is sensitive to wavelengths up to only 700 mμ, Berenblum and Chain's method (*Biochem. J.*, 1938, **32**, 286, 295) can be employed for determining 1 to 10 μg of P, readings being made at 635 mμ. For 0·5 to 4 μg of P, $SnCl_2$ should be used for reduction, and extraction should be performed with the min. vol. of *n*-butanol required for filling the cells in use, readings being taken at 700 mμ. If the spectrophotometer can be used for readings up to 900 mμ, the method of Horecker *et al.* (*J. Biol. Chem.*, 1940, **136**, 775), modified by an extraction with *n*-butanol, is suitable for determining 0·5 to 4 μg of P, readings being taken at 800 mμ. This is the preferred method and is recommended because it retains the high degree of precision of Fiske and Subbarow's method (*J. Biol. Chem.*, 1925, **66**, 375). The determination of organic P can thus be carried out after digestion with H_2SO_4 and H_2O_2 with no loss of P. The method is readily applicable for determining the ratio of cholesterol to phosphatides in lipoproteins after paper electrophoresis of serum, or for determining serum-free phosphatides after their separation by paper chromatography on paper impregnated with silicic acid. P. HAAS

1094. **Paper chromatography of urinary indoles.** J. B. Jepson (Courtauld Inst. Biochem., Middx. Hosp. Med. Sch., London). *Lancet*, 1955, **ii** (20), 1009–1011.—Urine (5-μl portions) is applied to the right-hand bottom corner of a 10-in. square sheet of Whatman No. 1 paper 3 cm from each edge, the spot being dried by a current of cold air between additions until 30 to 100 μl have been applied. The paper is chromatographed vertically with *iso*propyl alcohol - water - aq. NH_3 soln. (sp. gr. 0·880) (200:20:1 by vol.) for 16 hr. The paper is dried by a fan for 15 min. and chromatographed at right angles with butanol - water - glacial acetic acid (120:50:30 by vol.) for 6 hr. It is then dried by a fan for 30 to 60 min., dipped in 10 per cent. w/v *p*-dimethylaminobenzaldehyde in conc. HCl diluted with 4 vol. of acetone, held flat while the acetone dries and placed upon white paper for observation. The spots are outlined with lead pencil as they develop and their colour and order of appearance noted. The standard mixture run at the same time contains urea, potassium indoxyl sulphate, tryptamine hydrochloride, serotonin, creatinine sulphate and tryptophan (2 mg per ml of each). One drop of the standard mixture is sufficient, the urea, which is always present, providing a useful reference spot. H. F. W. KIRKPATRICK

1095. **Quantitative colorimetric estimation of Dibenamine in biological material.** K. H. Boltze, D. Weyland and H. Hofmann (Inst. Pharmak., Friedrich Schiller Univ., Jena, Germany). *Biochem. Z.*, 1955, **327** (3), 239–244.—Dibenamine (NN-dibenzyl-2-chloroethylamine) (**I**) can be estimated by the following colorimetric reaction. The aq. soln. of **I** (10 ml) is mixed with phosphate buffer (pH 5·2) (5 ml), bromocresol purple soln. (5 ml) and benzene (50 ml) and shaken for 2 min. After separation, the aq. phase is extracted again. Both the extracts are filtered and mixed, then extracted twice with 0·05 *N* NaOH soln. (10 ml) and the blue-violet NaOH extract is made up to 25 ml. The extinction is determined photometrically, with filter S59. The range of concn. measurable is 25 to 400 μg per 10 ml. The optimum pH is 5·2. Details are given of the application of this method to the determination of **I** in tissues, serum and urine. G. W. CAMBRIDGE

1096. **A new method of chromatographic differential micro-determination of bile acids in bile.** Tetsuzo Arima (Kyushu Univ. School Med., Fukuoka, Japan). *J. Biochem. Japan*, 1955, **42** (2), 169–179.—A chromatographic method of separating free from conjugated bile acids is described. The differential determination of tri- and di-hydroxycholanic acids in both free and conjugated types is effected by Murakami's method (*Ibid.*, 1952, **39**, 17) by the use of vanillin - phosphoric acid reagents. N. E.

1097. **Determination of deoxycholic and cholic acids.** M. Lambiotte (Inst. Biologie Physicochimique, Paris). *Bull. Soc. Chim. Biol.*, 1955, **37** (9–10), 1023–1030.—The method of Kaziro and Shimada for the determination of deoxycholic acid (*Hoppe-Seyl. Z.*, 1938, **254**, 57) has been modified to improve its reliability. According to the original procedure, the dried sample containing the acid is treated with 2 drops of benzaldehyde and 1 ml of 75 per cent. H_2SO_4; the product is heated to 50° C, then cooled, and 2 ml of glacial acetic acid are added. To ensure greater reproducibility of results, it is now recommended that the benzaldehyde and H_2SO_4 should be mixed before addition to the sample, which should be previously dissolved in a little ethanol in order to reduce a slight tendency to charring when heated. The mixture is heated on a water bath for 5 min., then cooled and 1·5 ml of ethyl acetate are added in place of the glacial acetic acid recommended by Kaziro and Shimada. The acid preserves the colour rather longer than the acetate, but a smaller quantity of acetate suffices, thus reducing loss of intensity of colour due to dilution. Immediately after completion of the reaction the extinction of the solution is measured at 615 mμ. Cholic acid is determined by measuring the extinction at 675 mμ of the colour produced when the dried sample, dissolved in glacial acetic acid, is heated with furfuraldehyde and 16 *N* H_2SO_4 for 30 min. on a water bath at 65° C. Cholic acid gives practically no absorption at 615 mμ. P. HAAS

1098. **Determination of α-oxoglutaric acid by column chromatography.** Setsuji Sakurai and Kinichi Sugae (Osaka Univ., Japan). *J. Biochem. Japan*, 1955, **42** (4), 367–373.—A colorimetric determination of α-oxoglutaric acid (**I**) as the 2:4-dinitrophenylhydrazone after chromatographic separation on silica gel is described. *Procedure*—An aq. soln. (1 ml) containing <1·5 micromoles of **I** is heated with 1 ml of 2:4-dinitrophenylhydrazine soln. (5 per cent. in 2 *N* HCl) at 37° C for 20 min., then extracted with 0·7 and 0·5 ml of purified ethyl acetate. The extract is poured on to a column of silica gel (4 g) previously wetted with 1·6 ml of the upper phase of a mixture of butanol - $CHCl_3$ - acetic acid - water (10:90:10:90). The chromatogram is developed with 10 ml of the lower phase of the solvent; the band of the 2:4-dinitrophenylhydrazone of **I** is eluted twice with 4 ml of ethyl acetate containing 1 per cent. of acetic acid; the absorption is measured at 400 mμ. Good agreement with the transaminase method was shown in the determination of **I** in products of the oxidative fermentation of glucose by *Escherichia coli*. N. E.

1099. **Paper-chromatographic separation and estimation of uronic acids.** F. G. Fischer and H. Dörfel (Chem. Inst., Univ. Würzburg, Germany). *Hoppe-Seyl. Z.*, 1955, **301** (4–6), 224–234.—A sharp separation of D-glucuronic, D-galacturonic and

D-mannuronic acids is possible by paper chromatography on Whatman No. 1 paper, with 5 to 50 μl of salt-free soln. in pyridine - ethyl acetate - acetic acid - water mixture (5:5:1:3 by vol.). Several chemical methods of freeing hydrolysates from mineral salts are given. The uronic acids may be detected and quant. estimated by reduction of triphenyltetrazolium hydroxide (*Anal. Abstr.*, 1955, **2**, 981). Glucuronic and mannuronic acids occur partly as lactones in hydrolysates. Lactones may be separated in pyridine - ethyl acetate - water (11:40:6 by vol.), but partial opening of the lactone ring takes place during development and only about 86 per cent. recovery is obtained in quant. determinations. Diuronic acids can be separated by the same solvent mixture as used for lactones. They can be eluted, hydrolysed and the constituents identified and estimated by a further chromatogram of the simple uronic acids. F. POWELL

1100. **Isolation and quantitative estimation of iodide, thyroxine and substances related to thyroxine by means of an anion-exchange resin.** P. Blanquet, R. W. Dunn and C. A. Tobias (Univ. Calif., Berkeley, California, U.S.A.). *Arch. Biochem. Biophys.*, 1955, **58** (2), 502–503.—In a study of the metabolism of ^{131}I, plasma or thyroid hydrolysates are poured on to a column (6 in. $\times$ $\frac{1}{2}$ in.) of Dowex-2 resin (200 to 400 mesh, regenerated before use with CO_3''-free 2 *N* NaOH, then with CO_2-free dist. water till the pH of the eluate is <8). After equilibration, elution is effected with 0·2 *N* HCl at 40 ml per hr. to a total of 500 ml. The eluate is collected and counted automatically in 1·5-ml fractions. Separate elution peaks are obtained for thyroxine, mono-, di- and tri-iodothyronines. W. H. C. SHAW

1101. **Detection and estimation of glucosamine and galactosamine on paper chromatograms.** F. G. Fischer and H. J. Nebel (Chem. Inst., Univ. Würzburg, Germany). *Hoppe-Seyl. Z.*, 1955, **302** (1), 10–19.—The estimation of amino sugars by treatment with acetylacetone and Ehrlich's reagent frequently gives erroneous results and fails to distinguish between glucosamine and galactosamine. Paper chromatography in pyridine - ethyl acetate - water - acetic acid (5:5:3:1 by vol.) or in phenol at pH 1 separates them from one another and from other saccharides and amino sugars. Quant. estimation may be carried out by ninhydrin or by reduction of triphenyltetrazolium hydroxide. The former method gives a lower paper blank and is less dependent on temp. but is less sensitive. In hydrolysates where protein-breakdown products may be found the formazan method is better. The material to be examined is hydrolysed with HCl, brought to a pH of 4 to 5 with silver carbonate and centrifuged. The supernatant liquid is used for chromatography. If only the sum of the two compounds is required, 3 to 4 hr. running suffices, but if individual values are required then 48 hr. is advisable. F. POWELL

1102. **Identification of neuraminic acid in histological sections.** P. B. Diezel (Path. Inst. Univ., Heidelberg). *Naturwissenschaften*, 1955, **42** (17), 487–488.—Neuraminic acid is a polyhydroxy amino acid with one hydroxy group oxidised to a carbonyl group, as in sugars. The acid reacts with Bial's reagent. Cleared paraffin or frozen sections are treated with acetone at 60° C for one hour, followed by an ether wash for one hour. The dry sections are then sprayed with Bial's reagent (40·7 ml of conc. HCl, 0·1 g of orcinol and 1 ml of 1 per cent. $FeCl_3$). Excess of reagent is allowed to run off and the slide is now held over a container of conc. HCl so that the acid fumes impinge on the section; this should be done in closed vessels for 30 to 60 min. in an oven at 60° C. The section is then air-dried. Areas rich in neuraminic acid stain red or, if very rich, a reddish violet. The colour fades slowly after 12 hours. Cerebral cortex from cases of infantile amaurotic idiocy is particularly rich in neuraminic acid; lipid-storing ganglion cells in gargoylism also react positive, and ganglion cells from normal cortex give a weak reaction. The corpora amylacea of the prostate and amyloid material give a very strong reaction. Other structures that give a positive reaction are heart muscle, smooth muscle of blood vessels, skeletal muscle, erythrocytes, granules of eosinophil leucocytes, the paramyeloid of myelomata, Russell's bodies, hyaline connective tissue, and the plaques in the cerebral cortex in cases of presenile dementia. E. KAWERAU

1103. **The rapid identification of adenine, adenosine, adenosine phosphoric acid and pyridine nucleotides on paper chromatograms.** E. Gerlach and H. J. Döring (Pharmakol. Inst. Univ., Heidelberg). *Naturwissenschaften*, 1955, **42** (11), 344.—The chromatograms are sprayed lightly with aq. 0·07 per cent. $KMnO_4$ soln. and hung immediately in an atmosphere of Cl for 15 sec., then dried for 5 min. at 100° C. This causes the wine colour to fade and all adenine- or adenosine-containing areas to appear as yellow or orange spots. Spraying with 3 *N* KOH then changes the colour to deep red; the background of the paper is white when dry. Moist NH_3 vapour should replace the KOH spray if the phosphate components are to be determined on the same sheet with molybdate reagent. The reaction is sensitive to 0·2 μg per ml and is specific for free nucleoside and nucleotide-bound adenosine. E. KAWERAU

1104. **Spectrophotometric analysis of nucleic acids in protein solutions and in crude organ extracts.** E. Annau (Animal Diseases Res. Inst., Hull, Que., Canada). *Canad. J. Biochem. Physiol.*, 1955, **33** (6), 1010–1017.—In continuation of previous work (*Anal. Abstr.*, 1956, **3**, 802) investigations have been made of mixed samples in which the absorption spectrum of one of the constituents has been limited, not as before by a reference soln. containing the respective sample, but by a reference soln. of a substance of a different chemical composition yet of an absorption max. similar to that of the sample. This amounts to a filter technique in which the elimination of the desired spectral regions is achieved by means of a selected reference soln. instead of glass filters. This has the advantage over filter photometry or an algebraic analysis of composite spectral curves of simplicity and the fact that the absorption gradients of the reference soln. can be experimentally adjusted to any value at a selected spectral region. By this method nucleic acids can be identified in mixed protein nucleic acid samples. Uric acid soln. of appropriate concn. were used as the reference standard. The method is also applicable to nucleoprotein complexes such as nucleohistone. P. HAAS

1105. **Investigations on leucocytes. II. Some chemical and physical properties of the deoxynucleic acids from haemolymphopoietic organs and from normal and leukaemic leucocytes.** E. Polli and G. Semenza (Ist. Clin. Med. Gen. e Terapía Med.,

Univ. Milan, Italy). *Biochem. Z.*, 1955, **327** (3), 231–238.—Details are given of the extraction of deoxynucleic acids from leucocytes and from tissues, and their estimation by infra-red spectrophotometry. Details are also given of the chromatographic separation of the products of acid hydrolysis, with subsequent identification by u.v. light, elution, and spectrophotometric estimation of the purine and pyrimidine bases. G. W. CAMBRIDGE

1106. **A method for the determination of trace amounts of histamine.** F. Schmidt and J. Gruhn (Phys. Chem. Inst., Friedrich Schiller Univ., Jena, Germany). *Naturwissenschaften*, 1955, **42** (13), 391–392.—In the coupling reaction with diazotised sulphanilic acid, glyoxalines undergo secondary reactions and the result is not strictly quantitative. The following conditions reduce side reactions to a minimum and render the method sensitive to amounts of 0·2 to 2·0 μg of histamine. Optimum colour reaction is obtained by coupling at a pH of 9·8 (borate buffer) at 0° C for 7 minutes. Ethanol is then added to stabilise the colour, which does not fade for several hours. E. KAWERAU

1107. **The isolation of histamine by paper chromatography.** F. Schmidt and D. Vorheier (Phys. Chem. Inst., Friedrich Schiller Univ., Jena, Germany). *Naturwissenschaften*, 1955, **42** (13), 392.—Partridge's solvent mixture of butanol - acetic acid - water was used in a one-dimensional ascending run for 15 hours or *iso*butyl alcohol saturated with 1 per cent. aq. NH_3 in a 20-hour run. The latter solvent gives the better separation of histamine from histidine. The papers are dried and sprayed, first with borate buffer of pH 11, then with diazotised sulphanilic acid. The histidine and histamine spots appear red, those of tyrosine and tyramine red - brown. A final spraying with 96 per cent. ethanol renders the spots semi-permanent. The substances can be eluted with dilute HCl in the region of their R_F values and the colour can then be developed in the eluate and quantitatively evaluated. Recoveries by this procedure amounted to between 90 and 96 per cent.; 0·1 μg of histamine can be detected by the reagent. E. KAWERAU

1108. **Estimation of free amino acids in biological material.** G. Gorbach, G. Dedic and E. H. Philippi (Inst. Biochem. Tech. Lebensmittelchem., Techn. Hochschule, Graz, Austria). *Hoppe-Seyl. Z.*, 1955, **301** (4–6), 185–190.—The pptg. agent used for removing proteins has considerable influence on the results of free amino-acid determinations in biological material. Five protein precipitants were tested by estimating the N in soln. of egg albumin, casein, blood fibrin and edestin before and after pptn. and the experiments were repeated after the addition of known quantities of six different amino acids. Trichloroacetic acid and calcium fluoride were found to ppt. only about two-thirds of the protein in egg albumin and fibrin, sodium tungstate gave only 80 per cent. pptn., but tungstophosphoric acid pptd. more than 90 per cent. in all instances and molybdophosphoric acid more than 99 per cent. Added basic amino acids were co-precipitated with protein when tungstophosphoric acid was used, but all the amino acids tested (histidine, arginine, alanine, valine, leucine and aspartic acid) remained in soln. when molybdophosphoric acid was the precipitant. F. POWELL

1109. **A ninhydrin reagent for quantitative amino-acid determinations on paper chromatograms.** J. Barrollier (Schering A.-G., Berlin). *Naturwissenschaften*, 1955, **42** (14), 416.—The more stable metal complex of the ninhydrin - amino-acid reaction product (dioxohydrindylidene-dioxohydrindamine) is formed directly by dipping the papers into a reagent prepared as follows—75 mg of $CdCl_2$ are dissolved in 6 ml of water, 0·3 ml of glacial acetic acid and 100 ml of acetone are then added, and 2·0 g of ninhydrin are dissolved in the mixture. Maximum colour development occurs after 24 hours at room temperature, and the red pigment, which has a maximum extinction at 509 mμ, can be eluted with methanol from the paper and obeys the Beer - Lambert law. E. KAWERAU

1110. **A sensitive reaction on paper of ninhydrin with hydroxyproline and proline.** T. W. Clarkson (Nuffield Dept. Occupational Health, Manchester Univ., England). *Biochim. Biophys. Acta*, 1955, **18** (3), 453–454.—The low sensitivity of ninhydrin for hydroxyproline (**I**) and proline (**II**) is overcome by the modification described. *Procedure*—Steam the developed chromatogram to remove adsorbed diethylamine (Redfield, *Biochim. Biophys. Acta*, 1953, **10**, 344) and dip in 0·1 per cent. w/v ninhydrin in benzene containing 0·1 per cent. v/v of collidine. When placed in dry steam for 1 min., **I** and **II** give magenta spots with red fluorescence in u.v. light. The limit of detection by fluorescence is 0·008 μg and 0·025 μg of amino nitrogen for **I** and **II**, respectively. W. H. C. SHAW

1111. **The rapid quantitative estimation of amino acids, particularly glutamic acid.** F. Schneider, R. Reinefeld and H. Müller (Inst. Landwirtschaft. Tech. u. Zuckerind., Brunswick, Germany). *Biochem. Z.*, 1955, **327** (3), 189–194.—By paper electrophoresis in 0·2 *N* acetate buffer, pH 3·8, at 270 V (10 V per cm) for 2 to 2·5 hr. the following amino-acid groups may be separated, aspartic, glutamic, neutral amino acids, γ-aminobutyric acid and basic amino acids. The spots are stained with ninhydrin and quant. evaluation may be made by photometric measurement. The extinction maximum for glutamic acid and γ-aminobutyric acid is 550 mμ, the error for glutamic acid being ±2 per cent. on amounts between 15 and 30 μg. For aspartic acid the extinction maximum is 570 mμ, the error being ±1·6 per cent. on 12·5 μg. For γ-aminobutyric acid the error is ±2·4 per cent. on 8 μg. G. W. CAMBRIDGE

1112. **Paper chromatography in routine determination of glutamic acid in production.** N. A. Khan, B. E. Baker and W. F. Van Horn (McDonald Coll., Que., Canada). *J. Agric. Food Chem.*, 1955, **3** (10), 853–855.—A procedure is described for the estimation of glutamic acid on buffered paper (pH 12) with phenol saturated with buffer (pH 12) and mixed with a small amount of butan-2-ol as solvent. There is clean separation of glutamic acid from the other amino acids, even in the presence of a high concn. of NaCl, and round compact spots of uniform size are formed. A heating period of 15 min. at 60° C is recommended for the rapid development of the ninhydrin colour. Results are compared with those obtained by Olcott's method. S.C.I. ABSTR.

1113. **Infra-red spectra of 3-phenyl-2-thiohydantoins of amino acids and their application to identification of N-terminal groups in peptides.** L. K. Ramachandran, A. Epp and W. B. McConnell (Nat. Res. Counc. Canada, Prairie Reg. Lab., Saskatoon, Canada). *Anal. Chem.*, 1955, **27** (11),

1734–1737.—The i.r. spectra of the 3-phenyl-2-thiohydantoins of 22 amino acids are presented. A characteristic spectrum was obtained for each compound tested and the parent amino-acid could therefore be positively identified. The N-terminal residues in five synthetic peptides were correctly identified by the use of these spectra. A modified method for the preparation of the phenylthiohydantoins of asparagine and glutamine is also described.
G. P. Cook

1114. **The identical behaviour of some peptides and amino acids in paper chromatography.** K. R. Deane and E. V. Truter (Leeds Univ., England). *Biochim. Biophys. Acta*, 1955, **18** (3), 435–436.—Direct one- or two-dimensional paper-chromatography is considered unreliable for identifying the free amino acids present in natural products because some peptides may behave similarly. The minimum requirement for proof of identity of amino acids is that chromatograms before and after hydrolysis should be identical; preferably single components should be hydrolysed and examined separately. In the particular cases studied, ninhydrin-reacting spots due to peptides were resolved after hydrolysis into six or more amino acids.
W. H. C. Shaw

1115. **An accurate method for the evaluation of proteins by electrophoresis.** E. B. M. De Jong (Klin. Chem. Lab. St. Elisabeth Krankenhaus., Tilburg, Netherlands). *Rec. Trav. Chim. Pays-Bas*, 1955, **74** (10), 1290–1300.—The method described involves the use of the dye Amidoschwarz 10 B (Amido black B) (**I**), which combines with serum proteins stoicheiometrically. The difficulty of washing out **I** from the paper is overcome by washing the strip with 1 per cent. acetic acid at 65° C in an apparatus which is described. The elution technique for evaluation of the proteins is recommended in preference to the spectrophotometric method since this latter technique is unreliable. The instability of **I** in NaOH soln., leading to inaccuracies, is shown to be caused by heavy-metal ions in the soln.; this difficulty is overcome by removing these cations with EDTA. The proteins on the electropherogram are stained with **I** and the excess of dye is washed out. The stained portions are cut out and eluted with 5-ml portions of a soln. containing aqueous *N* NaOH (500 ml), 96 per cent. alcohol (500 ml), and EDTA (0·5 g). The eluates are set aside for 10 min., then centrifuged to remove the filter-paper, and the extinction is measured at 630 mμ. By using this electrophoretic method the various serum proteins can be determined with the following limits of error: albumin, $\pm$0·5 per cent.; α_1-globulin, $\pm$0·3; α_2-globulin, $\pm$0·3; β-globulin, $\pm$0·3; γ-globulin, $\pm$0·4.
C. A. Slater

1116. **Fluorimetric determination of 0·1 to 10 micrograms of cholesterol [in animal tissues].** R. W. Albers and O. H. Lowry (Washington Univ. Sch. Med., St. Louis, Mo., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1829–1831.—The cholesterol is extracted from the tissue with ethanol and the extracts are evaporated to dryness. The residues are dissolved in a mixture of trichloroethane and acetic anhydride, and H_2SO_4 is added. The soln. are measured in a fluorimeter after being set aside for 1 to 2 hr. The method is applicable both to free and esterified cholesterol and no interfering substances have yet been encountered. The coefficient of variation is $\simeq$5 per cent. at the 0·1-μg level.
G. P. Cook

1117. **Microbiological synthesis of ergosterol. I. Assay procedure.** T. H. Stoudt and J. W. Foster. *Appl. Microbiol.*, 1954, **2**, 385–387.—Samples of fermentation broth (50 to 100 ml) are centrifuged. The solids are washed, centrifugally, with water several times to remove interfering materials and dried *in vacuo* or in air at 65° to 70° C for 20 hr. The dry residue is finely ground (to pass 80 mesh) and extracted (Soxhlet) for 6 hr. with ether. The extracts are evaporated to dryness at room temp. and, by three appropriate dilutions with chloroform, a final vol. containing 0·1 to 0·4 mg of ergosterol is prepared. To this are added 5 ml of the Liebermann - Burchard reagent and the mixture is maintained at $\simeq$25° C. The extinction is determined after exactly 10 min., with a 660-mμ filter, and again after exactly 20 min., with a 420-mμ filter. (Absorption max. at 670 mμ are reached in 2 min. at 25° C, and in 4 min. at 420 mμ.) If agreement between determinations at the two wavelengths is poor, that at 420 mμ is the more reliable. Additional confirmation of the result may be obtained by means of u.v. absorption data (max. at 285 and 296 mμ), the lowest value based on either wavelength being taken. Results of the colorimetric method showed coeff. of variation of 9·6 per cent.
A. G. Pollard

1118. **Infra-red spectra of steroids. II. The influence of the solvent on carbonyl frequency correlations.** W. Tarpley and C. Vitiello (Schering Corp. Sci. Res. Div., Bloomfield, N. J., U.S.A.). *Applied Spectroscopy*, 1955, **9** (2), 69–77.—An investigation has been made, with a double-beam spectrophotometer, into the influence of solvents on the frequencies of the carbonyl absorption bands in the infra-red spectra of 56 steroids. Published data for similar types of ketosteroids in CS_2 are confirmed and displacements caused by using CCl_4, $CHCl_3$, CH_2Br_2, $CHBr_3$ and mineral oil as solvents are tabulated. The magnitude of the shift towards lower frequencies in $CHCl_3$ and CH_2Br_2 was found to depend on the location and type of the carbonyl group.
P. T. Beale

1119. **The absorption spectra of steroids in "100 per cent." phosphoric acid.** W. J. Nowaczynski and P. R. Steyermark (Hôtel-Dieu Hospital, Montreal, Canada). *Arch. Biochem. Biophys.*, 1955, **58** (2), 453–460.—A new procedure for the determination and identification of steroids is based on the u.v. absorption characteristics of solutions in "100 per cent." phosphoric acid. Details of the absorption spectra for 34 steroids of the urinary and cortical series are given. For the two compounds examined quantitatively, extinction was proportional to concentration up to 25 μg of steroid per ml, and for ten compounds investigated the spectra were stable for at least 24 hr. The method had advantages over the use of conc. H_2SO_4 in reproducibility and stability. *Reagent*—Dissolve 79 g of P_2O_5 in 100 g (59 ml) of 85 per cent. H_3PO_4 (d = 1·7). Filter, after 30 min., through glass wool. *Procedure*—Heat the reagent to 100° C before use (to decrease viscosity) and add sufficient to the dry steroid to give a concn. of 25 μg per ml. Heat the solution in an oven at 107° $\pm$ 2° C for 20 min., stir well and fill a 1-cm silica cell with the solution. Measure the extinction over the range 220 to 600 mμ against a blank of the reagent heated similarly.
W. H. C. Shaw

1120. **Spectrophotometric determination of acid and alkaline phosphatases with o-carboxyphenyl phosphate. A comparison with the rate of cleavage**

of other substrates. H. Brandenberger and W. H. Weihe (Univ. Berne, Switzerland). *Helv. Chim. Acta*, 1955, **38** (6), 1347–1351.—The rate of enzymatic hydrolysis of *o*-carboxyphenyl phosphate (**I**) has been compared with that of other substrates commonly used for phosphatase determinations. An acid phosphatase from wheat germ hydrolysed **I** faster than β-glycerophosphate, phenyl phosphate, and phenolphthalein diphosphate. Two alkaline phosphatases hydrolysed **I** more slowly than β-glycerophosphate, but 10 times faster than phenolphthalein diphosphate. Even when another substrate is hydrolysed more rapidly, **I** is recommended because of the high accuracy and simplicity of the spectrophotometric determination described earlier by Brandenberger and Hanson (*Brit. Abstr. C*, 1953, 444). P. HAAS

See also Abstracts 1022, 1054, 1138, 1193, 1195, 1208.

Drugs

1121. **The photometric evaluation of alkaloids on paper chromatograms.** H. Thies and F. W. Reuther (Inst. Pharm. Lebensmittelchem. Univ., Munich). *Naturwissenschaften*, 1955, **42** (17), 486–487.—Bismuth sodium iodide dissolved in ethyl acetate gives a red colour with alkaloids. The reagent neither dissolves alkaloids nor causes their spread on the paper chromatogram. By using a filter with maximum transmission at 508 mμ, the blank absorption values of the alkaloid-free paper and reagent are reduced to a minimum. A powerful source of light is required when the reflectometric method for measuring density values is employed. The error in measuring the same spot was ±2 per cent. E. KAWERAU

1122. **Improved solvent mixtures for the separation of alkaloids by paper chromatography.** H. Thies and F. W. Reuther (Inst. Pharm. Lebensmittelchem. Univ., Munich). *Naturwissenschaften*, 1955, **42** (16), 462.—Esterification of solvent mixtures can be largely prevented by adding the corresponding ester to the solvent mixture. For example, papaverine and narcotine have distinct R_F values in a mixture consisting of butyl acetate, butanol, acetic acid and water (47:9:28:16), whereas in a solvent mixture that is in all respects identical, but with omission of the butyl acetate, their R_F values are identical. E. KAWERAU

1123. **Polarometric titrations of organic bases [alkaloids]. III. Titrations with picric, picrolonic, styphnic and flavianic acids and sodium alizarinsulphonate.** J. Zýka (Karlovy University, Prague, Czechoslovakia). *Českosl. Farmac.*, 1955, **4** (6), 301–305.—Picric acid at pH 4·6 to 7 and −0·4 V *vs.* the S.C.E. was suitable for the determination of papaverine (**I**), cinchonine (**II**) and strychnine (**III**), the error in each case being ±1 per cent. Flavianic acid can be used for quinine (**IV**) (error ±3 per cent.) and **II** (constant error of +5 per cent.) at pH 4·6 to 7 and −1·2 V. Sodium alizarinsulphonate gave good results with **I** (±1 per cent.), **IV** (±2 per cent.), and narcotine (±1 per cent.), but a constant error of −4 per cent., probably due to the solubility of the ppt., was obtained with **III**; a potential of −0·65 V was used, the titration medium being 0·3 *N* KCl adjusted to a pH of 4 to 6 (except for **I**, when 0·6 *N* KCl was used). Styphnic and picrolonic acids gave unsatisfactory results. A. O. JAKUBOVIC

1124. **Oscillographic polarography for the identification of opium alkaloids.** G. Dušinský (State Inst. for Control of Drugs, Bratislava, Czechoslovakia). *Českosl. Farmac.*, 1955, **4** (8), 400–404.—The alkaloids studied were papaverine (**I**), apomorphine (**II**), morphine (**III**), diacetylmorphine (**IV**), ethylmorphine, codeine, thebaine and narcotine. For oscillographic polarography, **I** and **II** can be used directly; **III** and **IV** have to be oxidised [with $K_3Fe(CN)_6$] and then examined in alkaline soln. (1·25 *N* NaOH). The remainder can be studied in alkaline soln. without prior oxidation, but cannot be differentiated, as they each give a similar depression in the polarographic curve at 1·5 V. The method is rapid and sensitive, *e.g.*, 0·4 mg of **I** can be detected in a 300-fold excess of **III**. A table of voltages at which the depressions occur in the polarography of the various alkaloids is given, as well as figures showing the oscillographic polarograms for some of the compounds and their mixtures. A. O. JAKUBOVIC

1125. **Cinchona. II. Assay of the extract.** K. S. Manudhane and M. L. Khorana (Univ. Bombay, India). *Indian J. Pharm.*, 1954, **16** (11–12), 218–219.—The new procedure described is based on the pptn. of the majority of the non-alkaloidal emulsifying substances by the addition of CaO. *Procedure*—The extract (5 ml) is weighed accurately and macerated with 0·5 g of CaO. The ppt. is washed with hot ethanol until free from alkaloids, the filtrate and washings being acidified with H_2SO_4 and the ethanol removed by boiling. The residual acid soln. is filtered through a plug of cotton wool and then extracted with $CHCl_3$. The acid liquor is made alkaline and extracted with $CHCl_3$, and the extract is washed and evaporated to dryness at 100° C. The total alkaloids are weighed. The method gives concordant results about 2·5 per cent. higher than those of the B.P.C. assay. H. B. HEATH

1126. **The detection of apoatropine and belladonnine in atropine.** E. I. Rosenblum and W. S. Taylor (Development Division, Drug Houses of Australia, Melbourne). *J. Pharm. Pharmacol.*, 1955, **7** (12), 1067–1071.—Apoatropine (**I**) and belladonnine (**II**) are both more toxic than atropine (**III**), and may be formed during the manufacture of **III** from natural sources. The B.P. 1953 and U.S.P. XIV ammonia tests and the U.S.P. platinic chloride test are sensitive tests for **II**, but allow the presence of up to 3 per cent. of **I**. The B.P. test for readily oxidisable substances in hyoscine hydrobromide, in which 0·1 *N* $KMnO_4$ is used, will detect 0·1 per cent. of **I** in **III**. A. R. ROGERS

1127. **Paper-chromatographic and biological properties of reserpine and related compounds.** R. J. Boscott and A. B. Kar (Medical School, Univ. Birmingham, England). *Nature*, 1955, **176**, 1077–1078.—Paper-chromatographic procedures are recommended for checking the purity of commercial samples of *Rauwolfia* alkaloids and determining the composition of complex mixtures of the alkaloids used for therapeutic purposes and in pharmacological tests. A number of suitable developing solvents and detection tests are described. Best results were given by a solvent prepared by just saturating 10 per cent. v/v acetic acid in aq. 5 per cent. Na acetate with *n*-butyl ether; the clear aqueous phase was used. Detection of <1-μg amounts of reserpine and rescinnamine was effected by fluorescence after spotting the paper with 3 per

cent. sodium nitroprusside in 50 per cent. trichloroacetic acid, or by fluorescence 30 min. after spotting the paper with micro droplets of 90 per cent. H_2SO_4 and later spraying with 9 per cent. Na_2CO_3 soln. The alkaloid zones were shown as intense blue, green or greenish-blue spots.

O. M. WHITTON

1128. **Gaseous phase of cigarette smoke. Isolation and analysis for total aldehydes.** G. P. Touey (Tenn. Eastman Co., Kingsport, Tenn., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1788–1790.—A simple method for isolating smoke gases from the liquid - solid components during automatic smoking is described. A special filter removes >99 per cent. of the liquid - solid phase and also allows the gases to pass into absorption flasks for analysis. The determination of aldehydes is based on their reaction with dimedone (5:5-dimethyl*cyclo*hexane-1:3-dione) to form insol. bisdimedone derivatives. Recoveries of various aldehydes from known soln. ranged from 80 to 99·5 per cent. and the apparent aldehyde content of four brands of cigarettes was found to be 0·8 to 0·9 mg per cigarette.

G. P. COOK

1129. **The paper-chromatographic separation of the glycosides of *Digitalis purpurea* L.** C. Günzel and F. Weiss (Pharm. Inst., Humboldt Univ., Berlin, Germany). *Z. anal. Chem.*, 1955, **148** (4), 250–251.—As a supplement to a previous paper (*cf. Anal. Abstr.*, 1954, **1**, 1341), reverse-phase chromatography of 10-μg amounts of purpurea glycosides A and B, digitoxin, gitoxin and diginin on silicone-treated paper is described. Anisaldehyde - acetic acid - sulphuric acid reagent is used to identify the bands.

A. R. ROGERS

1130. **Identification, separation and determination of digitalis glycosides. II. Separation and determination of individual lanatosides and deacetyllanatosides in lanatoside ABC.** O. Hrdý, Z. Jung and A. Šlauf (State Inst. for Control of Drugs, Prague, Czechoslovakia). *Československ. Farmac.*, 1955, **4** (8), 395–400.—The separation is achieved by paper chromatography. The glycosides (50 to 100 μg), dissolved in ethanol, are placed on paper, which is then saturated with formamide soln. (**I**). The developing is carried out with chloroform for degluco- and deacetyldegluco-lanatosides, and with chloroform - ethyl acetate (8:2) for deacetyllanatosides. The developer is always saturated with **I**, and separation is observed by the light of a mercury lamp. The fluorescing glycoside spots are cut up, treated on the paper with xanthhydrol reagent, extracted with hot water, and the extinctions (measured with a Pulfrich photometer, filter S53) are compared with those of standard soln. The determination is quant. (even with <10 μg), is not affected by the presence of **I**, and no substance is lost by adsorption and retention on the paper. The maximum error is ± 5 per cent.

A. O. JAKUBOVIC

1131. **Circular-paper chromatography of insulin.** Z. Pádr, J. Urbanková and S. Jehlička (Res. Inst. Pharmacy and Biochem., Prague, Czechoslovakia). *Československ. Farmac.*, 1955, **4** (6), 311–313.—After referring to current paper-chromatographic methods, the radial method used is described in detail. Whatman No. 1 paper (30 cm in diam.) is used. Six 100 to 200-μg samples (in acidified 50 per cent. ethanol) are placed along the circumference of a circle of 1·5 cm radius from the centre of the paper. The chromatogram is developed with a mixture of *n*-butanol, acetic acid and water (3:1:3) for 36 hours. Protamine, if present, remains at the centre and the position of the insulin front is illustrated in several figures. Results for a no. of preparations are discussed. The method is applicable to the determination of purity of cryst. insulin or injections, as well as to manufacturing control.

A. O. JAKUBOVIC

1132. **The use of chromatography and polarography in the evaluation of insulin solutions for injections.** M. Voldan (State Inst. for Control of Drugs, Prague, Czechoslovakia). *Československ. Farmac.*, 1955, **4** (8), 407–409.—To isolate the insulin, paper chromatography of the soln. was carried out on Whatman No. 4 paper impregnated with a 0·5 per cent. soln. of NaCl. The chromatogram was developed with a mixture of amyl alcohol, butyl alcohol, glacial acetic acid and water (0·6:2·4:1:3·5), with the addition of 1 per cent. of amyl acetate to the alcohol layer to improve sharpness of the insulin zone. For the detection, acidic dyestuffs were used, in particular, bromocresol green. The colorimetric determination of the insulin, both on the paper and after elution, is described. For polarography, 1 ml of the diluted injection soln. (1:1) (adjusted to pH 2·75) was added to 20 ml of a mixture of 0·00064 *N* $CoCl_2$, 0·1 *N* NH_4Cl and 0·1 *N* aq. NH_3. The purity of the soln. is given by a function of the angle of the polarographic wave. The results by the two methods are in good agreement with one another and with biologically obtained figures.

A. O. JAKUBOVIC

1133. **Chemical estimation of penicillin in pharmaceutical preparations. I. Penicillin ointments.** F. Neuwald and G. Ulex (Lab. Kgl. priv. Apotheke, Schönberg, Germany). *Arch. Pharm. Berlin*, 1955, **288** (8–9), 432–438.—Three methods are described for the determination of penicillin in different ointment bases, containing other antibiotics, sulphonamides, etc. *Procedures*—(*a*) The ointment (2 g $\equiv$ 2000 i.u. of penicillin) is dissolved in 40 ml of benzene and extracted once with 20 ml and twice with 10 ml of a 20 per cent. NaCl soln., and the combined aq. penicillin extract is filtered and made up to 50 ml with NaCl soln. To 25 ml of this soln. is added 1 ml of *N* KOH and, after 20 min. at 19° to 20° C, 5 ml of a buffer soln. (acetic acid 2·4 g, Na acetate 5·44 g in 100 ml of water) (pH 4·6), 1 ml of *N* HCl and 10 ml of 0·01 *N* I soln. After 20 min., the excess of I is titrated with 0·01 *N* $Na_2S_2O_3$, with starch as indicator. Blank estimations are carried out similarly on the remaining 25 ml of penicillin soln., without treatment with *N* KOH and neutralisation with *N* HCl, but rinsing with 5 ml of the buffer soln. The difference between the results of the blank and the main determination $\times$ 0·4455 $\equiv$ mg of sodium penicillin, calc. as $C_{16}H_{17}O_4N_2SNa$. (*b*) The ointment (4 g $\equiv$ 4000 i.u. of penicillin) is extracted as in (*a*), when 25 ml of the penicillin - NaCl soln. are extracted with 25 ml of $CHCl_3$, the pH is adjusted to 2 with H_3PO_3 (10 per cent.) (0·4 ml), for 2 min., then the $CHCl_3$ extract is dried over anhyd. Na_2SO_4. A 20-ml portion of this soln. is shaken with three 5-ml portions of 0·1 *N* KOH, the alkaline soln. is filtered and, after 10 min., is treated with 1·5 ml of *N* HCl soln., 5 ml of acetate buffer soln. and 10 ml of 0·01 *N* I soln., then back-titrated as under (*a*). (*c*) Penicillin is isolated from 5 g of ointment ($\equiv$ 5000 i.u. of penicillin) as in (*b*), the $CHCl_3$ extract (25 ml) is dried, the $CHCl_3$ is removed by distillation, and the

cooled residue is treated with a nitration mixture (10 g of KNO_3 in 100 g of H_2SO_4) on a water bath for 30 min.; 2 ml of water are gradually added while cooling in an ice bath. Then 2 ml of 25 per cent. aq. NH_3 soln. are added dropwise, and the soln. is mixed and allowed to reach room temp., when 2 ml of a hydroxylamine soln. (15 g of $NH_2OH.HCl$ in 100 g of water) are added, followed by a further 5 ml of aq. NH_3 soln., and set aside for 45 min. Photometric measurements are made at 550 mμ and the results are compared with a calibration curve obtained with a standard sample of sodium benzylpenicillin. Blank determinations are also required. The methods give an accuracy of 91·5 to 99·6 per cent. G. R. WHALLEY

1134. **Separation of the tetracyclines by paper chromatography.** H. Fischbach and J. Levine (Food and Drug Admin., Washington, D.C., U.S.A.). *Antibiot. & Chemother.*, 1955, **5** (11), 640–642.—A simple rapid procedure is described for the identification and differentiation of chlortetracycline, oxytetracycline and tetracycline. Development on Whatman No. 1 paper slightly damp with water is by an ascending technique with a mixture of 2 vol. of formic acid and the separated organic phase from a mixture of *n*-butyl acetate, *iso*butyl methyl ketone, *n*-butanol and water (5:15:2:22). The chromatograms are air-dried and sprayed with 5 per cent. $FeCl_3$ in methanol. W. H. C. SHAW

1135. **A turbidimetric method of assay of tyrothrycin.** J. Kramer and A. Kirshbaum (Food and Drug Admin., Washington, D.C., U.S.A.). *Antibiot. & Chemother.*, 1955, **5** (10), 561–565.—The rapid sensitive turbidimetric method described is based on the inhibition of growth of *Streptococcus faecalis* (A.T.C.C. 10541) in a conventional penicillin-assay medium. A standard curve is established from the turbidities (measured photo-electrically) produced after incubation for 3 hr. at 37° C in the presence of 0·008 to 0·032 μg of standard tyrothrycin per 10 ml of medium. Test solutions diluted to about 0·020-μg dose level are assayed with a standard error of 0·0006 μg. Detailed extraction procedures are given for various types of pharmaceutical preparations. Bacitracin, neomycin and antiseptics that may also be present do not interfere.
W. H. C. SHAW

1136. **Paper chromatography of local anaesthetics.** J. Reichelt (Pharm. Control Inst., Prague, Czechoslovakia). *Českosl. Farmac.*, 1955, **4** (6), 297–301.—The current paper-chromatographic methods are reviewed and a new one is described. Whatman No. 1 or 3 paper is impregnated with 40 per cent. formamide in ethanol and dried. Fifty-μg quantities of the substance were used and the spots were developed with either benzene, benzene - chloroform (60:40), or chloroform vapour. Detection was by examination under u.v. light or by spraying either with *p*-dimethylaminobenzaldehyde or with Dragendorff's reagent. Chromatograms are shown for each of the developer systems. A table is given showing the best developer and best method of detection for each of the 20 compounds examined. A. O. JAKUBOVIC

1137. **The determination of *iso*amyl α-2-diethylaminoethylaminophenylacetate ("Adopon").** Toshio Iwasaki and Yaichi Matsushima (Dept. Pharmacol., City Medical School, Osaka, Japan). *J. Osaka City Med. Center*, 1955, **4** (2), 113–117.—"Adopon" (**I**) is extracted from an aq. soln. saturated with $NaHCO_3$ (pH 8) with 1:2-dichloroethane (**II**) and treated with a saturated aq. soln. of methyl orange. The aq. layer is separated and the amount of methyl orange in **II**, which is equiv. in amount to the **I**, is colorimetrically determined in acid soln. For the deproteinisation of biological materials, the use of Na_2WO_4 is suitable. K. SAITO

1138. **Micro-determination of isoniazid.** J. Wagner, P. Kraus, B. Večerek (Research Inst. Tuberculosis, Prague, Czechoslovakia). *Českosl. Farmac.*, 1955, **4** (8), 389–392.—The known methods for the determination of isoniazid (**I**) are comprehensively reviewed. The new method described is based on the reduction of mercury potassium iodide by the hydrazine group, at pH > 10, preferably in 0·25 to 1 *N* NaOH soln. The orange - yellow soln. produced turns greenish yellow on being acidified, and is measured colorimetrically or nephelometrically. An acid medium is preferred for the measurement of extinction since, although low values are given, ammonium salts do not interfere. For determining **I** in blood serum, the serum is first deproteinised with $ZnSO_4$ and $Ba(OH)_2$. Hydrazine chloride and sulphate give extinction coeff. similar to those obtained with **I**, but 2:4-dinitrophenylhydrazine and phenylhydrazine hydrochloride give only half these values. The method is sensitive to 2·5 μg in 1 ml and is subject to errors of ±8 per cent. The determination of **I** in tablets and in injections is also described. A. O. JAKUBOVIC

1139. **Bromimetry of 4-hydroxycoumarin and its bis-derivatives in glacial acetic acid.** G. Dušinský (State Institute for Control of Drugs, Bratislava, Czechoslovakia). *Chem. Listy*, 1954, **48** (12), 1868–1869.—The determination of 4-hydroxycoumarin (**I**), dicoumarol (**II**) and Pelentan (ethyl biscoumacetate) (**III**) by potentiometric titration with Br in acetic acid was studied. In the absence of Na acetate as catalyst only **I** reacts, requiring 2 equiv. of Br. In the presence of Na acetate the determination of the three compounds can be carried out either directly, or by adding an excess of Br and back-titrating the excess with Na_3AsO_3 (**I** and **II** require 8 equiv., **III** 6 equiv. of Br). To determine **II** and **III** in commercial preparations, dissolve the sample (0·02 to 0·1 g) in hot glacial acetic acid (20 ml), add, after cooling, a saturated soln. of Na acetate in glacial acetic acid (3 ml) and titrate with a 0·1 *N* soln. of Br in the same solvent. The equivalence point is marked by the appearance of a permanent yellow tint. One ml of a 0·1 *N* Br soln. corresponds to 0·01681 g of **II** and to 0·0204 g of **III**. The accuracy is ±0·5 per cent. Alternatively, add an excess of the Br soln. and back-titrate with 0·1 *N* Na_3AsO_3 after 20 min. Under these conditions 1 ml of 0·1 *N* Br is equiv. to 0·0042 g of **II** and 0·0068 g of **III**; the accuracy is ±2·5 per cent. G. GLASER

1140. **Analysis of the antihistamines. IV.** E. W. Neuhoff and H. Auterhoff (Inst. Pharmaz. Lebensmitt. Chem., Univ. Würzburg, Germany). *Arch. Pharm. Berlin*, 1955, **288** (8–9), 400–407.—Qual. colour reactions and physical characteristics are given for a number of commercial antihistamine compounds, together with u.v. absorption data. Identification tests include their reaction with fuming HNO_3, Ehrlich's reagent, chloramine and HCl followed by NH_3, 10 per cent. chloramine soln. and $CHCl_3$, diazo reagent (D.A.B. VI), vanadium sulphate reagent (D.A.B. VI), $KMnO_4$ and satd. Na_2CO_3 soln. G. R. WHALLEY

1141. **Polarographic method of determining saccharin.** M. B. Neĭman (Inst. Chem. Physics, Acad. Sci. USSR, Moscow). *Zh. Anal. Khim., SSSR*, 1955, **10** (3), 175–179.—The polarographic behaviour of saccharin in various solutions has been studied. The determination in 0·1 *N* KCl or 0·1 *N* HCl is satisfactory. G. S. SMITH

1142. **The use of paper chromatography in pharmacopoeial tests. The determination of sucrose in glucose.** S. Vach and F. Horák (Control Lab. Medika, Plzeň). *Českosl. Farmac.*, 1955, **4** (6), 310.—The sulphuric acid test for detecting sucrose in glucose was found to be unsatisfactory and insensitive; a paper-chromatographic method is described. Glucose (100 mg) was dissolved in 10 ml of water; 0·01 ml of the soln. was placed on Whatman No. 4 paper and developed for ≃4 hr. with butanol - acetic acid - water (4:1:5). The chromatogram was then dried at 80° C and developed with aniline oxalate. The R_F value for sucrose is 0·1 and for glucose 0·21. A. O. JAKUBOVIC

1143. **Paper-chromatographic examination of tinctures and fluid extracts included in the D.A.B. VI.** L. Hörhammer and K. W. Leue (Inst. Pharmaz. Arzneimittel., Univ., Munich). *Arch. Pharm. Berlin*, 1955, **288** (8–9), 377–388.—Tinctures and fluid extracts from the D.A.B. VI are examined by paper chromatography, with 58 cm × 60 cm strips and a *n*-butanol - acetic acid - water (4:1:5) system, in a water-saturated atmosphere, 0·1 ml of a tincture and 0·05 ml of a fluid extract being applied to the paper. After separation, the strips are treated with one of three developing soln.—a saturated methanolic soln. of $Al_2(SO_4)_3$, a saturated soln. of borax, or 5 per cent. KOH in 50 per cent. methanol soln., and the fluorescence is then examined under a quartz lamp. The R_F values and a description of the separated zones, etc., are given for a number of tinctures. G. R. WHALLEY

1144. **A test for the mechanical strength of compressed tablets.** A. R. Webster and N. J. Van Abbé (Genatosan Ltd., Loughborough, Leics., England). *J. Pharm. Pharmacol.*, 1955, **7** (11), 882–890.—An apparatus is described for testing the friability of tablets. It consists of a glass tube (6 in. × 1 in.) in which a specified number of tablets are shaken mechanically by an eccentric for 2 min.; fine powder is allowed to sift out through a 12-mesh 22-gauge wire screen, and the loss in weight of the tablets is measured. Consideration of the errors of the test suggests that the mean of four successive determinations should be taken. A. R. ROGERS

1145. **An improved test for uniformity of weight of tablets.** K. L. Smith (Boots Pure Drug Co. Ltd., Nottingham, England). *J. Pharm. Pharmacol.*, 1955, **7** (11), 875–879.—The method of sequential analysis is used to provide an alternative procedure to that of the B.P. 1953 for testing the uniformity of weight of tablets. Uniform batches can be accepted with fewer weighings than are required by the official test, and the rigid division between acceptance and rejection in borderline cases is removed. The procedure is particularly suited to routine control by the manufacturer. A. R. ROGERS

1146. **Toxicological analysis.** A. S. Curry (Home Office Forensic Science Lab., Harrogate, England). *J. Pharm. Pharmacol.*, 1955, **7** (12), 969–989.—This is a review with 194 references of modern aspects of toxicological analysis, with particular reference to the use of paper chromatography and u.v. spectrophotometry. The identification of poisons in the following groups is discussed. *Volatile in steam from acid soln.*—alcohols, halogenated hydrocarbons, acetone, acetaldehyde, cyanides, compounds of P, etc. *Volatile in steam from alkaline soln.*—nicotine, amphetamine. *Non-volatile*—metals and heat-stable anions. *Extracted from ether soln. by $NaHCO_3$ soln.*—aspirin metabolites and other organic acids. *Extracted from ether soln. by NaOH soln.*—barbiturates, hashish, phenolic anthraquinones, Warfarin, phenylbutazone. *Non-basic and not extracted from ether by alkali*—phenacetin, apiol, insecticides, etc. *Extracted from aq. NH_3 soln. by ether*—most alkaloids. *Extracted from aq. NH_3 soln. by $CHCl_3$ or a mixture of $CHCl_3$ and propan-2-ol*—xanthines, glycosides. *Ionised compounds not extracted from aq. soln. by solvents*—quaternary ammonium salts, amino acids, rodenticides. A. R. ROGERS

1147. **Analytical scheme for the detection of poisons in suspect foods.** M. Arcangel Guatelli. *Rev. Asoc. Bioquim. Argentina*, 1955, **20**, 67–78; *Monit. Farm.*, 1955, **61**, 365–369; 385–389.—A general scheme is outlined. The examination is carried out in three parts, (*a*) for volatile poisons, (*b*) for inorganic poisons, and (*c*) for organic poisons. L. A. O'NEILL

1148. **Toxicological detection of barbiturates by paper chromatography.** M. Ledvina, B. Chundela, B. Večerek and K. Kácl (Karlovy Univ., Prague, Czechoslovakia). *Českosl. Farmac.*, 1955, **4** (8), 386–388.—Micro-analytical methods are reviewed and their difficulties discussed. A paper-chromatographic method is described in which the developed chromatograms are photographed under u.v. light at 254 mμ, with a 2-mm UGS filter and a 30-mm chlorine filter. The best developer is a mixture (2:1) of amyl alcohol and 20 per cent. aq. NH_3 soln., although it has the disadvantage of slow development. Some barbiturates in quantities down to 10 μg can be identified by the shift in the absorption maximum on the addition of 0·5 *N* NaOH soln. The analytical characteristics of a number of barbiturates are tabulated. A. O. JAKUBOVIC

See also Abstracts 1165, 1166, 1167.

Food

1149. **Examination of commercial foodstuffs. IV. The use of Potterat and Eschmann's complexiметric method for sugar estimations after selective fermentation by van Voorst's method.** H. Hadorn and H. Suter (Laboratorium VSK, Basle). *Mitt. Lebensmitt. Hyg., Bern*, 1955, **46** (4), 341–355.—Lactose and maltose in sugar mixtures and commercial foodstuffs were estimated by titration with Fehling's solution or by Potterat and Eschmann's complexiметric method, after selective fermentation with *Saccharomyces cerevisiae* and *Candida pseudotropicalis*, respectively. The second method gave slightly low results if dextrin was present. W. H. PARR

1150. **Rapid sugar-extraction procedure for analysis of candied fruits, jams and fresh fruits.** J. A. Kitson, C. C. Strachan and R. F. Cain (Fruit and Veg. Processing Lab., Summerland, B.C., Canada). *J. Agric. Food Chem.*, 1955, **3** (10), 862–864.—A rapid sugar-extraction procedure based on the use

of a Waring Blendor was adapted to the analysis of candied fruits, jams and certain fresh fruits. The standard A.O.A.C. method of determination was also slightly modified by the pre-extraction neutralisation of natural acids and the substitution of citric acid in place of HCl. *Procedure*—Transfer a 50-g aliquot of the ground mixed sample to a previously cooled blender jar; add ice-cold water (250 ml), ice (60 to 70 g) and 2 to 3 drops of octan-2-ol. Blend for 2·5 min. then add a further 60 to 70 g of ice and continue blending for 2·5 min. Transfer the contents to a 500-ml calibrated flask and adjust to vol. at 20° C. Rinse the blender with two small portions of the macerate, discard each, then pour into the blender the remainder of the contents of the flask; blend for 1 to 2 sec. with sufficient long-fibre acid-washed asbestos to fill a 100-ml beaker. Filter the resulting slurry through a 9-cm coarse-porosity sintered-glass filter. Dilute suitable aliquots (20 to 100 ml) of the filtrate to 500 ml for the determination of reducing sugars by the A.O.A.C. method, and total sugars after inversion. The rapid method is claimed to have equal precision and accuracy when applied to candied fruits and fresh frozen strawberries, apricots and prunes, but gives higher total sugars in jams. The process takes 1 hr. to complete. H. B. HEATH

1151. **The determination of mustard oils [*iso*thiocyanates] in rape-seed meal.** L. R. Wetter (Nat. Res. Council Canada, Prairie Regional Lab., Saskatoon, Canada). *Canad. J. Biochem. Physiol.*, 1955, **33** (6), 980–984.—The method described is a modification of that of Viehoever, Clevenger and Ewing (*J. Agric. Res.*, 1920, **20**, 117), according to which the mustard oil (allyl *iso*thiocyanate) reacts with ammonia to form a substituted thiourea, and the thiourea, in ammoniacal $AgNO_3$, breaks up into a monosubstituted carbodiimide and insol. Ag_2S. The excess of $AgNO_3$ is determined by the Volhard method, the *iso*thiocyanate content of the mustard oil being calculated as allylcarbinyl *iso*thiocyanate (**I**) (1 ml of 0·1 *N* $AgNO_3$ ≡ 0·005659 g of **I**). The crude myrosinase needed to set free the *iso*thiocyanate from the glucoside in the rape-seed is prepared by extraction of white mustard seed in a Soxhlet apparatus, the fat-free powder being used. *Procedure*—Approximately 2 g of rape-seed meal and 0·4 g of crude enzyme are thoroughly masticated with 100 ml of citrate buffer (pH 4·0) and shaken for 3 hr. in a tightly stoppered flask; 10 ml of 95 per cent. ethanol are then added and the liquid is immediately distilled into 10 ml of 0·1 *N* $AgNO_3$ and 2·5 ml of 10 per cent. aq. NH_3. The distillate of 70 ml is heated under a reflux condenser in a boiling-water bath for 30 min., then filtered and made up to a known vol.; the excess of $AgNO_3$ is determined in the usual way. Although the assay is not completely quant. (88 to 93 per cent.) the values determined for various rape-seed meals are comparable. P. HAAS

1152. **The detection and quantitative determination of colouring materials in butter and margarine.** H. M. Espoy and H. M. Barnett (Barnett Lab., Long Beach, California, U.S.A.). *Food Tech., Champaign*, 1955, **9**, 367–372.—Quantitative methods of assaying the pigments found in butter and margarine, without the necessity of saponification, are described. *Procedure*—Melt a cube of the sample and centrifuge off the oil. Weigh accurately 30 to 35 g of the oil and dissolve in hexane to make 100 ml (**I**). Identify the pigments as follows. Shake a small portion of **I** with conc. HCl; a red colour in the aq. phase indicates coal-tar colours yellow AB and OB (FD & C yellow 3 and 4). Shake a further portion with aq. NH_3 (5 per cent.) in ethanol (55 per cent.); a straw colour in the aq. phase indicates annatto. If a yellow coloration remains in the hexane phase in each case, carotene is present. *Assay for carotene*—Pass 15 ml of **I** through a column (15 mm × 150 mm) packed with a mixture of equal parts of MgO and filter-aid (Hyflo Supercel); elute the column with hexane - acetone (9:1) (30 ml) and collect the eluate in a 50-ml calibrated flask. Read the absorption at 450 mμ ($E^{1\%}_{1\,cm}$ for β-carotene = 2520). *Assay for coal-tar colours*—Add 15 ml of **I**, by pipette, into a separating funnel containing hexane (15 ml) and extract with 3 × 5 ml of ice-cold H_2SO_4 (60 per cent. w/w). Separate each acid portion into a second funnel containing 50 ml of ice-cold water and 50 ml of ether; shake thoroughly and discard the acid layer; wash the ether layer twice with dil. aq. NH_3 and finally with water until free from acid; filter through Na_2SO_4 and evaporate off the solvent. Dissolve the residue in *cyclo*hexane and adjust the vol. to 25 ml. Dilute to 50 ml and read the absorption at 435 mμ ($E^{1\%}_{1\,cm}$ for the pure dye = 585). *Assay for annatto extract*—Pass 15 ml of **I** through a column packed with a mixture of equal parts of Na_2CO_3 and filter-aid. Add 10 ml of hexane, followed by 10 ml of acetone. When the acetone has been drawn through the column add 10 ml of ethanol (70 per cent. v/v) and start collection of the eluate when the colour is near the bottom of the column. Collect about 10 ml of eluate and adjust to 10 ml with ethanol (70 per cent.). Filter the soln. if necessary and read the absorption at 455 mμ ($E^{1\%}_{1\,cm}$ for bixin = 3200). From visual comparisons 1 g of β-carotene ≡ 0·5 g of bixin ≡ 3·5 g of coal-tar colours. H. B. HEATH

1153. **Estimation of saccharin in prepared tea.** M. C. Sen Gupta, M. S. Madiwale and J. G. Bhatt (Haffkine Inst., Bombay). *Indian J. Pharm.*, 1955, **17** (9), 185–190.—Kastle's reaction for the detection of saccharin by its reaction with phenol to form phenol red has been developed into a quant. method. Data indicate that the method when carried out on pure saccharin yields accurate and reproducible results, which agree closely with those of the B.P.C. method. O. M. WHITTON

1154. **Colour and turbidity measurements in wort and beer by a new Zeiss electrophotometer.** H. Hecht (Inst. Ferment. Techn., Technical College, Munich). *Brauwissenschaft*, 1955, **8** (9), 207–214; (10), 235–240.—An investigation of the possibilities of the Elko II electrophotometer (*cf. Anal. Abstr.*, 1956, **3**, 843, including comparisons of the results obtained with those given by the iodine- and Brand-scale classifications and other methods, shows that reliable colour measurements of wort and beer can be made at 380 or 420 mμ, and turbidity measurements at 750 mμ. A formula is given for the correction of colour measurements for observed turbidities. The turbidity measurements are not affected by the colour of the wort or beer. These findings are supported by tabulated data. Measurements of colour and turbidity by the Elko II apparatus and by various other methods are given

for a large number of worts and beers. Colour measurements of wort should be made within 1 hr. of running-off in order to avoid complications due to darkening. Iodine-scale values for worts obtained by the apparatus are slightly higher than those obtained by visual comparison. The Elko II. apparatus gives reproducible results and is convenient in use. P. S. ARUP

1155. **Determination of higher alcohols.** J. Mejane and –. Cathy (Centre d'Application et de Recherches de l'E.N.I.A., Douai, France). *Industr. Agric. Aliment.*, 1955, **72** (7–8), 475–480.—Five methods for the detection or determination of higher alcohols in distilled spirits are described and compared. (*i*) The "official" method, based on a qual. test, is carried out by mixing 100 ml of sample (diluted to 50 per cent. v/v) with 1 ml of aniline and 1·2 ml of H_3PO_4 (sp.gr. 1·71), refluxing for 1 hr., cooling, distilling, slowly adding 10 ml of H_2SO_4 (sp. gr. 1·83) to 10 ml of the first 75 ml of cooled distillate and heating at 120° C for 1 hr. No colour should develop. This test detects 6 to 7 g per hectolitre of higher alcohols. (*ii*) The "improved official" method is based on the same procedure as (*i*), but any colour developed is compared with similarly prepared standards containing 1, 2, 3, etc., g per hectolitre of *iso*butyl alcohol. (*iii*) The Komarowsky method is based on adding 1 ml of an alcoholic soln. of salicylaldehyde and 20 ml of H_2SO_4 (66° Bé) to 10 ml of sample (50 per cent. v/v), mixing, standing for 1 hr. and measurement of the colour developed against a series of prepared standards. (*iv*) The "modified" Komarowsky method is based on (*iii*), but the sample tested is 96 per cent. v/v and the time of standing is 2 hr. instead of 1 hr. (*v*) In the "Von Fellenberg modification" of the Komarowsky method, in which 1 per cent. alcoholic *p*-hydroxybenzaldehyde is used instead of the salicylaldehyde, the vol. of sample tested is 10 ml (at 50 per cent. v/v), and 10 ml of H_2SO_4 are added; the mixture is heated at 100° C for 20 min., the comparison tubes with the mixture are immediately cooled in ice and the colours compared immediately. The results of a series of analyses with these methods are reported and it is concluded that the unmodified Komarowsky method (*iii*) is best. S.C.I. ABSTR.

1156. **Sorbic acid, a new preservative: its detection in beverages.** R. G. Eeckhaut (Lab. de Chimie. et de Bactériol., Quai Baudeloo, Ghent, Belgium). *Fermentatio*, 1955, (3), 136–142.—The following method is specific for sorbic acid, and will detect smaller quantities (0·7 p.p.m.) than are required for efficient preservation. *Procedure*—Distil a mixture of the sample (100 ml), water (50 ml) and tannic acid (3 g), collect 100 ml of distillate and test a small portion with aq. 1 per cent. $FeCl_3$; a violet coloration indicates the presence of sorbic or salicylic acid. Extract the organic acids with ether, then into alkaline soln. (10 ml) by the usual method and evaporate this soln. to half its bulk. To the cooled soln. add 5 ml of 25 per cent. (by vol.) H_2SO_4 and 1 ml of 0·1 *N* $KMnO_4$. Decoloration occurs within 1 min. in the presence of both the acids, but sorbic acid can be distinguished from salicylic acid because it yields acetaldehyde on oxidation, which can be detected by distilling off 1 ml of the soln. into 2 ml of water, and testing the liquid in the receiver with Schiff's reagent. Negative results are obtained for preservatives other than sorbic acid, but a positive result is obtained with cinnamic acid (a weak preservative). P. S. ARUP

1157. **Preservatives containing mercury, and their detection in beverages.** R. G. Eeckhaut (Lab. de Chimie et de Bactériol., Quai Baudeloo, Ghent, Belgium). *Fermentatio*, 1955, (3), 119–135.—A method by which 0·15 p.p.m. of Hg can be detected in beer is described and is used to detect a preservative containing sodium azide and Na mercurihydroxybenzoate. *Procedure*—Evaporate the sample (500 ml) to half its bulk, destroy all the organic matter with $KClO_3$ and HCl in the presence of a trace of $CuSO_4$, and remove free Cl by the addition of Na_2SO_3. Precipitate the Hg as HgS by the addition of Na_2S, filter, dissolve the ppt. in hot HCl plus HNO_3, dilute the soln. with 150 ml of water and filter again. After the addition of a little Na_2SO_3 and methyl orange, adjust the pH of the filtrate and washings to 3. Immerse a spiral of $\simeq$15 cm of fine brass wire in the soln. and set aside during 48 hr. for the deposition of the Hg on the wire. The Hg is detected by known methods. P. S. ARUP

1158. **Detection of fluoroacetic acid in foods.** Iwao Kawashiro and Keishiro Okubo. *Bull. Nat. Hyg. Lab., Tokyo*, 1954, **72**, 171–174.—To detect fluoroacetic acid the thioindoxyl reaction for monohaloacetic acid (Ramsey and Clifford, "Methods of Analysis, A.O.A.C.," 6th Ed., 1945, Sect. 29.22) is applied. *Procedure*—Make 20 ml of an extract soln. slightly alkaline, evaporate to 5 to 10 ml, acidify slightly, extract with ether and re-extract with a slightly alkaline soln. For a solid sample powder, acidify weakly, extract with ether and re-extract with a slightly alkaline soln. In the colour reaction evaporate the alkaline extract just to dryness, add 5 to 10 drops of 1·5 per cent. *o*-mercaptobenzoic acid in 0·1 *N* NaOH and 5 drops of 50 per cent. NaOH soln., mix, evaporate to dryness on a water bath, heat for 1·5 hr., dissolve in a little water, add 1 ml of 2 per cent. $K_3Fe(CN)_6$ soln. and mix well. (In the presence of CH_2ICOOH a red colour is obtained.) To detect F′, apply the Al haematoxylin method (*cf.* Okuno, *Chem. Abstr.*, 1947, **41**, 3235). If F′ are present the colour of Al haematoxylin at pH 7 deteriorates gradually. CHEM. ABSTR.

1159. **Spectrophotometric method for determining piperine in oleo-resins of black pepper.** H. J. Fagen, E. P. Kolen and R. V. Hussong (Kraft Foods Co., Glenview, Ill., U.S.A.). *J. Agric. Food Chem.*, 1955, **3** (10), 860–862.—The chemical method for the evaluation of the piperine content of oleo-resins of black pepper is based on the determination of total N by the Kjeldahl method. It is shown that soln. of pure piperine in $CHCl_3$ exhibit absorption max. at 260, 310 and 345 mμ, the last being the principal peak. A sample of pure piperine is prepared as follows. To 100 g of oleo-resin of black pepper add light petroleum (500 ml), stir well and filter. Dissolve the ppt. in a min. quantity of hot ethanol, filter and crystallise. Recrystallise three times from hot absolute ethanol (m.p. 130° C). This sample was used in the preparation of a standard graph. *Assay procedure*—Accurately weigh $\simeq$0·25 g of the oleo-resin and transfer it to a 100-ml calibrated flask with $CHCl_3$ and adjust to vol. Transfer by pipette a 0·5-ml aliquot into another 100-ml calibrated flask and adjust to vol. with $CHCl_3$.

Read the absorption at 345 mμ in a spectrophotometer, with a 1-cm quartz cell, against $CHCl_3$ as blank. Dilute soln. of piperine in $CHCl_3$ are photosensitive and the reading should be carried out immediately. The percentage of piperine in the sample is determined from the standard graph. This method gave results averaging 2·24 per cent. higher than a polarographic method and 11·39 per cent. lower than the normal Kjeldahl method, probably owing to the presence of other nitrogenous bodies. H. B. HEATH

1160. **Research on the unsaponifiable matter of oils and some fats. Determination of hydrocarbons, squalene and sterols.** A. Fabris and M. Vitagliano (Inst. Agric. Res., Naples Univ., Italy). *Ann. Sper. Agr.*, 1955, **9**, 625–659.—Existing methods for the examination of olive oil (**I**), with particular reference to the detection of adulteration, are surveyed. The determination based on the high iodine value of squalene (**II**) in the unsaponifiable matter (**III**) is the best guide to the purity of **I**. The following chromatographic method is given, in which saponification time, size of oil sample and drying conditions are standardised. *Procedure*—Saponify 20 g of **I** with 6 g of KOH and 80 ml of 95 per cent. ethanol for 2 hr. Transfer the hot soln. into a 500-ml separating funnel, wash the saponification flask with 200 ml of light petroleum and add the washings to the separating funnel. Mix the layers, cool, add 80 ml of H_2O, allow to settle, re-extract the aq. portion with 50 ml of light petroleum, wash the combined extracts with alcohol at 50° C, add phenolphthalein to the light-petroleum layer, neutralise, and dry over anhydrous Na_2SO_4. Distil the solvent from a tared flask, dry the residue of **III** at 100° C for 15 min., cool and weigh. Prepare a column of Al_2O_3 and add the light-petroleum soln. of **III**, which, except for the hydrocarbons, is absorbed, giving an orange band (carotene); weigh the hydrocarbons contained in the eluate after evaporation of the solvent and drying at 100° C for 15 min. Determine **II** by the iodine uptake of **III**, with iodine monobromide (Hanus reagent). The method was used on 117 samples of genuine **I**; **III** varied between 200 mg per cent. and 750 mg per cent. and **II** between 124 mg per cent. and 692 mg per cent. It is concluded that **II** is not a reliable guide to the adulteration of **I**, but will indicate the presence of **I** in other oils or fats.
H. A. FISHER

1161. **A chemical method for the determination of vitamin D with the aid of stannous chloride.** H. Tschapke and H. Plessing (Anstalt Vitaminforsch. Vitaminprüfung, Potsdam-Rehbrücke). *Naturwissenschaften*, 1955, **42** (14), 417.—Stannous chloride dissolved in acetyl chloride yields a yellow pigment with pure vitamin preparations (D_2 and D_3) in chloroform solution. Vitamin A gives a blue colour with the reagent and must be separated from the mixture by chromatography on a column of activated bentonite; cholesterol, 7-dehydrocholesterol and ergosterol do not interfere with the test. Irradiated preparations have a reddish tinge which does not interfere with the determination. *Procedure*—Freshly distilled acetyl chloride (10 ml) is added to 0·1 g of $SnCl_2$ in a glass-stoppered test-tube (16 mm × 160 mm); the mixture is shaken for 1 min., allowed to stand for 1 min. and filtered. The filtrate should be clear and colourless. To 2 ml of the chloroform solution of the vitamin add 1 ml of the reagent and shake and, after 2·5 min., transfer the solution to a colorimeter cup that can be closed with a lid and measure the extinction at 550 mμ against a reagent blank. The colour reaches its maximum within 3 min. and remains constant for 6 min. The calibration with pure vitamin D_2 gives a straight line. Good agreement has been obtained with biological assay methods. E. KAWERAU

1162. **Quantitative separation of B vitamins by electrophoresis on agar plates.** G. Marten (Landw. Untersuchungs- u. Forschungs-anstalt Kiel, Gutenbergstr. 77, Germany). *Nature*, 1955, **176**, 1064–1066.—A method is described for determination of the components of a mixture of group-B vitamins by direct electrophoresis in thin layers of agar jelly. High-voltage electrophoresis (up to 10,000 V) is carried out in silicon films. After separation in the electric field, a second layer (*B*) of agar jelly is placed on the first (*A*). Layer *B* contains all the substances required by the test organisms seeded into the agar except that to be determined. Zones of growth appear in those spots corresponding to the presence of the vitamin or its active derivative in layer *A*. The logarithm of the dose is directly proportional to the diameter of the growth zone. A method combining electrophoresis and paper chromatography for increased separation of active growth factors is described. Growth zones obtained with *Lactobacillus fermentum* ATCC 9338 demonstrated as little as 0·002 μg of thiamine, the intact thiamine molecule being required. *Rhodotorula mucilaginosa* demonstrates the pyrimidine content alone. *Phycomyces blakesleeanus* responds to higher concentrations of the thiazole moiety, but not to pyrimidine. In the presence of small quantities of thiazole, the mould develops a mycelium on those spots containing pyrimidine, or conversely forms it with small amounts (4 mg per 100 ml of medium) of pyrimidine on spots containing thiazole. O. M. WHITTON

1163. **The estimation of vitamin B_1 in pharmaceutical products.** J. J. Doherty, N. Cane and F. Wokes (Ovaltine Research Lab., King's Langley, Herts., England). *J. Pharm. Pharmacol.*, 1955, **7** (12), 1053–1061.—The u.v. absorption of vitamin B_1 (**I**) shows an isosbestic point at 273 mμ over the pH range 1 to 9, which may be used in a spectrophotometric method of assay. Assays of B.P. injections by this method agree well with those by the fluorimetric and gravimetric methods before and after exposure to light and heat, and it is recommended that an improved fluorimetric or spectrophotometric method should supplement the official gravimetric method for the analysis of small amounts of material. There is no evidence, physical, chemical or microbiological (*Ochromonas malhamensis*), that development of a yellow colour on exposing **I** to light is accompanied by significant loss of activity. *Spectrophotometric method*—Dilute two aliquots of the sample with 0·1 *N* HCl (pH 1) and phosphate buffer of pH 7, respectively, to a concn. of $\simeq$10 μg per ml, and measure the extinctions at 245 mμ and 273 mμ in 1-cm cells. Subtract ΔE_{273} from ΔE_{245} (where ΔE is the increase in E produced by changing the pH from 7 to 1) and multiply by 50 to give the concn. of anhydrous **I** in μg per ml. A. R. ROGERS

1164. **Characterisation and determination of vitamin-B_1 phosphoric esters. I. Biological methods.** G. de la Fuente Sánchez (Inst. Esp. Fisiol. y Bioquím., Madrid, Spain). *Inf. Quím. Anal.*, 1955, **9** (5), 153–158.—Thiamine pyrophosphate (cocarboxylase) (**I**) is determined by manometric measurement of the rate at which it effects the

catalytic decarboxylation of pyruvic acid, in the presence of purified carboxylase or yeast cells deprived of co-enzyme and bivalent cation. Calibration curves are constructed with known amounts of chromatographically purified synthetic **I**. The method is specific for **I** and 0·05 to 10 μg per ml may be determined to within ± 2 per cent.
L. A. O'NEILL

1165. **A simple microbiological assay method for vitamin B_{12} in liver extracts.** A. N. Bose (Bengal Immunity Res. Inst., Calcutta). *Indian J. Pharm.*, 1955, **17** (10), 203–209.—A rapid and reproducible agar-cup assay, with *Lactobacillus leichmannii*, has been developed for the determination of vitamin B_{12} in purified and fractionated liver extracts. Five dilutions each of the sample and standard are arranged on the same plate so that high concn. are not adjacent, and incubated at 38° C for 24 hr.; the assay is done in triplicate and the results are determined graphically. High results due to alkali-stable factors in certain samples can be corrected by preliminary short-time (3-hr.) ascending chromatography on paper with water-saturated *iso*butyl alcohol, followed by a 4-point assay, with eluates of the original spots. For proteolysed liver extracts, *Escherichia coli* mutant is used in a 4-point assay, and the effects of the alkali-stable material are reduced by diluting the samples to contain 0·005 μg or less of vitamin B_{12} per ml.
S. C. JOLLY

1166. **The chemical and microbiological determination of vitamin B_{12} in liver extracts.** I. Carneri. *Il Farmaco, Sci. Ed.*, 1955, **10** (1), 31–36.—A chemical method for the determination of vitamin B_{12} (**I**) is described and compared with microbiological methods. *Procedure*—To a vol. of liver extract containing $\simeq 100$ μg of **I** add 1 per cent. by wt. of NaCN. After 5 hr. at a pH of 10, conversion of **I** into the dicyano complex is complete. Add Na_2SO_4 to give a 20 per cent. concn., extract 3 times with a total of 15 ml of benzyl alcohol and centrifuge to break the emulsion and remove impurities. To the alcoholic extracts add 7·5 ml of $CHCl_3$, extract 3 times with a total of 12·5 ml of H_2O, make the vol. of the extracts up to 12·5 ml and filter. To one 5-ml portion of soln. add 1 ml of aq. NaCN (10 per cent.); to another 5-ml portion add 1 ml of aq. KH_2PO_4 (12·5 per cent.). Filter and determine spectrophotometrically the difference of the extinctions of the two soln. at 582 mμ in 10-mm cells. Results generally agree with those obtained by microbiological methods and are claimed to be superior as they eliminate errors due to the presence of biologically active impurities. H. A. FISHER

1167. **Microbiological determination of the B_{12} vitamins by means of the phytoflagellate "*Euglena gracilis* isol. T".** H. C. Heinrich, G. Rädel and L. Sommer (Physiol.-chem. Inst., Univ. Hamburg). *Z. Vitam.- Horm.- u. Fermentforsch.*, 1955, **7** (2–3), 124–127.—By replacing *Euglena gracilis* var. *bacillaris* by a more recently acquired strain *Euglena gracilis* var. *saccharophila*, isol. T, the sensitivity of the method for the assay of vitamin B_{12} is greatly increased and the incubation period is reduced from 10 to 18 days, required by the earlier strain, to from 7 to 14 days. The method is recommended for the microbiological determination of B_{12} vitamins in biological material, commercial products and in investigation of vitamin-B_{12} metabolism.
P. HAAS

See also Abstracts 1141, 1147.

Sanitation

1168. **Substitution of *o*-tolidine by tetramethylbenzidine in the determination of chlorine in water.** L. M. Kul'berg and L. D. Borzova. *Zavod. Lab.*, 1955, **21** (8), 920–921.—Tetramethylbenzidine, $(CH_3)_2NC_6H_4C_6H_4N(CH_3)_2$, a synthesis of which is given, is preferred to *o*-tolidine for determining Cl in water since the orange colour obtained is better for observation in artificial light. It is used in the same way as *o*-tolidine. G. S. SMITH

1169. **A spectrophotometric determination of iodine in natural waters.** Ken Sugawara, Tadashiro Koyama and Kikuo Terada (Nagoya Univ., Nagoya, Japan). *Bull. Chem. Soc. Japan*, 1955, **28** (7), 494–497.—The iodine is first pptd. with $AgNO_3$ soln., a large quantity of AgCl acting as a co-precipitant, then oxidised to iodate with Br. The iodate is treated with CdI_2, when six times the amount of iodine contained in the original sample is liberated, and is determined spectrophotometrically as the starch - iodine complex.
G. R. WHALLEY

1170. **Apparatus for determination of dissolved sulphide and iron in river waters.** A. B. Wheatland and G. F. Lowden (Water Pollution Res. Lab., Stevenage, England). *Chem. & Ind.*, 1955, (46), 1469–1470.—In the apparatus described, suspended solids are removed by filtration in an inert atmosphere to avoid loss of hydrogen sulphide. Hydrogen sulphide is then displaced from the filtrate with acid, absorbed in zinc acetate soln., and measured iodimetrically, or colorimetrically as methylene blue, according to the quantity of sulphide present. Dissolved iron in the sample is determined by analysis of an aliquot of the filtrate.
S.C.I. ABSTR.

See also Abstract 1184.

Agriculture and Plant Biochemistry

1171. **The separation of plant proteins by high-tension paper electrophoresis.** G. Schneider and G. Sparmann (Botan. Inst. Justus Liebig Hochschule, Giessen, Germany). *Naturwissenschaften*, 1955, **42** (13), 391.—Vegetable protein from various sources can be split into a number of fractions by electrophoresis in diluted Sorensen's borate buffer at a pH of 11·5 when a voltage of 1500 V is employed. Plant press-juice of various components of rye, sugar beet, soyabean seeds, etc., have been analysed.
E. KAWERAU

1172. **Qualitative determination of lignin oxidation products by chromatography on paper impregnated with sodium tetraborate.** D. E. Bland and C. Stamp (Div. Forest Products, C.S.I.R.O., Melbourne, Australia). *Aust. J. Appl. Sci.*, 1955, **6** (3), 353–358.—Vanillin (**I**), 4-hydroxy-3-methoxyacetophenone (acetovanillone) (**II**), syringaldehyde (**III**), 4-hydroxy-3:5-dimethoxyacetophenone (acetosyringone) and *p*-hydroxybenzaldehyde can be separated by ascending chromatography on paper impregnated with 0·05 *M* aq. sodium tetraborate, with a mixture of either methanol - *iso*propyl ether - water (1:1:1 by vol.) or methanol - benzene - water (7:7:10 by vol.) as solvent. The spots are revealed in u.v. light. Three drops (each of 0·005 ml) of a 1 per cent. soln. in ethanol of the solids obtained from a chloroform extraction of the original sample are applied to the paper. **I**, **II** and **III** are determined quant. by elution of the spots (cut

from the paper) with methanol, followed by spectrophotometric measurement of the extinction of the solutions at 300 mμ. W. J. BAKER

1173. **Rapid colorimetric estimation of soil copper employing a sodium diethyldithiocarbamate - salt mixture.** S. N. Edson and L. E. Watson (Univ. Florida, Gainesville, U.S.A.). *Chemist Analyst*, 1955, **44** (4), 94–95.—Extracts (5 ml) of the soil in sodium acetate solution (prepared by dissolving 5 g of NaOH in 500 ml of H_2O, adding 11 g of glacial acetic acid and diluting to 1 litre with H_2O) are tested with 0·05 g of a dry mixture (1 + 99) of Na diethyldithiocarbamate and NaCl in the presence of 0·3 ml of buffer solution (prepared by dissolving 67·9 g of NH_4Cl in 300 ml of H_2O, adding 570 ml of conc. aq. NH_3, and diluting to 1 litre with H_2O) which prevents interference from Fe and Ca. The colour developed after 1 min. is compared against standards or the extinction is measured in a photometer, with a blue filter. Beer's law is valid for 0·2 to about 10 p.p.m. of copper. The blue filter prevents interference from Mn in alkaline solution. Interference from minute amounts of Ni, Co and Bi in soil extracts is not significant.

O. M. WHITTON

1174. **Determination of nitrate and ammonia in soil.** J. M. Bremner and K. Shaw (Rothamsted Exp. Sta., Herts., England). *J. Agric. Sci.*, 1955, **46**, 320–328.—To the soil sample (10 to 50 g) is added *N* K_2SO_4 (2 ml per g) (containing H_2SO_4 sufficient to produce pH 1·0 to 1·5 in the extract). For highly organic soils the proportion of extractant is increased. The soil suspension is shaken mechanically for 2 hr. and filtered (Whatman No. 32). An aliquot (*e.g.*, 4 ml) of the extract containing up to 100 μg of ammonia N is placed in the outer chamber of a modified Conway micro-diffusion apparatus and 1 ml of 2 per cent. boric acid containing the Conway - O'Malley indicator (*Biochem. J.*, 1942, **36**, 655) in the inner chamber. Approx. 3 ml of a freshly prepared suspension of light MgO (12 per cent. w/v) are added to the outer chamber, the apparatus is sealed, and the contents of the outer chamber are mixed. After incubation at 25° C for 24 hr. the NH_3 in the boric acid solution is titrated with 0·005 *N* H_2SO_4. Nitrate plus NH_3 in another aliquot of the extract is determined similarly, except that 1 ml of $Ti_2(SO_4)_3$ solution [15 ml of 15 per cent. w/v technical $Ti_2(SO_4)_3$ containing 23 per cent. w/v of H_2SO_4, diluted to 50 ml with water] is added to the outer chamber before the MgO. The contents of the outer chamber are mixed several times during incubation. Recovery of N (50 μg) added to an extract averaged 99·8 per cent. (NH_3) and 99·9 per cent. (NO_3'). Among labile compounds of N examined only glutamine was decomposed (max. 3·6 per cent.) under the prescribed conditions to an extent >1 per cent. The presence of NO_2' in extracts lowered the values for NO_3' but not for NH_3. This effect can be eliminated by the addition of sulphamic acid to the extract (0·2 g per 100 ml). Phosphate (10 mg of P as KH_2PO_4) did not interfere with determinations of NH_3 or NO_3' (100 μg in each case). A. G. POLLARD

1175. **Colorimetric field test for organic matter in mineral soils.** S. N. Edson and R. H. Mills (Coll. of Agric., Univ. Florida, Gainesville, U.S.A.). *J. Agric. Food Chem.*, 1955, **3** (10), 852–853.—The method is based on the determination of the residual Cl after the soil sample has been shaken with chlorine soln. for 1 min. and allowed to stand for 5 min. The suspension is filtered and to 2 ml of the clear filtrate, collected in a test-tube (16 mm × 150 mm), three drops of a prepared *o*-tolidine soln. are added; the liquids are mixed and the intensity of the yellow colour developed after the soln. has been standing for 15 min. is proportional to the amount of org. matter oxidised. The method is accurate to ±0·5 per cent. and results of tests on 18 soil samples compare favourably with those by the standard chromic acid method.

S.C.I. ABSTR.

5.—GENERAL TECHNIQUE AND LABORATORY APPARATUS

General

1176. **Pneumatic valve for liquids.** J. Pinkava and O. Wichterle (Považské chem. závody, Žilina, Czechoslovakia). *Chem. Listy*, 1954, **48** (12), 1850–1858.—The device consists essentially of a float chamber containing a glass float which closes a ground-glass seat with a glass ball. The flow of the fed liquid is regulated by gas (compressed air) pressure. The valve can be used with advantage to feed liquids into systems at pressures lower or higher than atmospheric, or against varying pressures. The accuracy is ±1·5 per cent.

G. GLASER

1177. **A constant-rate feeding device for liquids.** J. Pinkava and V. Kaláb (Považské chem. závody, Žilina, Czechoslovakia). *Chem. Listy*, 1954, **48** (12), 1858–1862.—The all-glass apparatus consists of a float chamber, two volumetric reservoirs and an outflow channel, all inter-connected by a system of solenoid-controlled valves in such a way that while one reservoir is being filled the other empties. An electric impulse counter is incorporated in the circuit and the construction compensates for volume changes due to temperature. The device, accurate to within 0·066 per cent., is suitable for the feeding of both pure and turbid or contaminated liquids at a constant rate. G. GLASER

1178. **Improved apparatus for the quantitative absorption of gases in liquids.** W. E. Golding and A. W. Ellis (North Thames Gas Board, Beckton, London). *Chem. & Ind.*, 1955, (44), 1401–1402.—An apparatus is described which is used to determine small amounts of SO_2 in gas streams. Gas passes into the absorbing liquid (*e.g.*, for SO_2, 10-vol. H_2O_2) contained in a cylinder fitted with an inner central tube, through which the passage of gas forces the absorbing liquid and sprays it over glass balls which form a peripheral packing between the inner tube and the walls of the cylinder; the liquid returns to its original location through a drain tube situated below the gas-inlet tube. The lower part of the cylinder, into which the base of the inner tube, the gas inlet and the drain tube all lead, is, except for these orifices, sealed by a transverse glass septum from the upper part, which contains the glass balls and also the gas-outlet orifice. The top of the cylinder is closed with a ground-glass stopper, and the base is connected to a ground-glass stopcock, enabling the apparatus to be emptied, washed out and recharged without being disconnected from the analysis train. S.C.I. ABSTR.

1179. **Magnetically actuated glass pump for circulating gases.** R. J. Brunfeldt and V. C. F. Holm (Phillips Petroleum Co., Bartlesville, Oklahoma, U.S.A.). *J. Chem. Educ.*, 1955, **32** (10), 528.—A pump for recirculating gaseous reactants through reaction zones or absorbents (*e.g.*, in studying the reducibility of metal oxides with H) is operated by a glass piston which has a core of soft iron wire sealed within it and is moved to and fro by two alternately energised solenoids. The piston is enclosed in a tube which runs laterally across two parallel sides into which the gas circuit is divided at this point. On each of these sides are two spherically ground valves, one behind and the other ahead of the junction with the piston tube, *i.e.*, four valves in all, which make pumping action effective with each movement of the piston by appropriately synchronised opening and closing.
S.C.I. Abstr.

1180. **Determination of gas by continuous weighing: application to the kinetics of the thermal dissociation of cupric bromide.** P. Barret (Faculté des Sciences de Dijon, France). *Bull. Soc. Chim. France*, 1955, (10), 1146–1152.—In the apparatus described, inert gas at a constant rate and carrying the vapour to be absorbed passes through a rigidly fixed tube (13 to 15 mm diam. and 150 mm long), which fits without friction between concentric metal spirals holding absorbent and fitted into a wider tube of thin glass (28 mm internal diam. and 135 mm long). The outer tube, spirals and absorbent are fixed on the balance pan and concentricity with the fixed tube is assured by means of adjusting screws on the pan suspension. The tube was tested satisfactorily for absorption of Br on C without loss and for CO_2 on Ascarite with $Mg(ClO_4)_2$ with losses <1 per cent. The balance is adapted for continuous recording on photographic paper by means of a small mirror on the beam, the movement of the balance giving a range of 200 mg. The effect of the constant gas stream and the damping by the concentric tubes is discussed. The system has been successfully used for studying the kinetics of decomposition of $CuBr_2$.
E. J. H. Birch

1181. **Simple apparatus for handling radioactive barium carbonate obtained by wet combustion.** R. B. Duff and A. H. Knight (Macaulay Inst. Soil Research, Craigiebuckler, Aberdeen). *Chem. & Ind.*, 1955, (46), 1469.—The apparatus is designed for the oxidation of ^{14}C-labelled materials by the Van Slyke - Folche wet-combustion reagents, and its essential feature is an absorption tube fitted with a sintered-glass filter (porosity 3) at the base outlet to enable pptd. $BaCO_3$ to be filtered off and washed with a minimum of manipulation in an atmosphere of nitrogen. S.C.I. Abstr.

1182. **Integrated set of laboratory fractionators for routine analytical distillations.** G. M. Cooke and B. G. Jameson (Imperial Oil Ltd., Sarnia, Ontario, Canada). *Anal. Chem.*, 1955, **27** (11), 1798–1803.—A new all-glass laboratory fractionator has been designed that has advantages over existing apparatus of greater speed, higher attainable temperatures and lower space requirements. D. G. Higgs

1183. **A simple laboratory vacuum-gauge.** G. Wagner and L. Ottendorfer (Inst. Anorg. Anal. Chemie, Tech. Hochsch., Vienna). *Öst. ChemZtg*, 1955, **56** (5–6), 77–78.—Directions are given for constructing a simple Pirani-type gauge suitable for measuring pressure in the range 10^{-3} to 1 mm (Hg). The indicator resistance is the filament of a 7-watt electric light bulb, in one arm of a Wheatstone bridge type of circuit, supplied with 220 V d.c. stabilised to 0·2 V. The milliammeter is calibrated against a McLeod gauge.
A. R. Rogers

1184. **A method for determining aero-allergen concentrations with the molecular filter membrane.** S. Cryst, C. W. Gurney and W. Hansen. *J. Lab. Clin. Med.*, 1955, **46** (3), 471–475.—A description is included of the construction of an automatic sampling apparatus suitable for collecting pollen grains and other air-borne particulate matter, greater than 0·2 μ in size, for predetermined periods during 24 hr. W. H. C. Shaw

1185. **"Chromatobox" and "pherobox", apparatus for paper chromatography and electrophoresis.** J. Barrollier (Schering A.-G., Berlin). *Naturwissenschaften*, 1955, **42** (17), 486.—The "chromatobox" (7 cm × 7 cm × 4 cm) is capable of accommodating a paper strip 6 cm × 40 to 50 cm. The strip is rolled up with a sheet of plastic material acting as apron in roll-film fashion. The protruding end of paper dips into a solvent reservoir, which is partitioned off from the main compartment. The "pherobox" is constructed on the same principle, except that the paper strip is rolled up between an outer and inner layer of plastic material; the base of the apparatus is divided into the two buffer compartments. Endosmotic effects are reduced to a minimum by impregnating the paper ends with collodion before use. E. Kawerau

1186. **Set-up for two-dimensional paper-chromatography.** E. C. Mathew and B. M. Das. *J. Chem. Educ.*, 1955, **32** (7), 352.—Details are given for the construction of a simple laboratory apparatus (including container), which has given useful results for vegetable tannins. A. Ledwith

1187. **An improved method in circular-paper chromatography.** N. C. Ganguli (Univ. Coll. Sci. and Tech., Calcutta, India). *Naturwissenschaften*, 1955, **42** (17), 486.—The filter-paper from which the wick is made is T-shaped, the horizontal bar is 20 mm × 5 mm and the vertical bar 20 mm × 3 mm. When this paper is rolled up, the thick portion assures a firm hold in the centre hole of the circular paper, though the tongue for the ascending supply of solvent is still no more than 3 mm wide. E. Kawerau

1188. **Electromagnetic device for shortening the equilibration period in paper chromatography.** M. J. Head and R. J. Canaway (Grassland Res. Inst., Hurley, Berks., England). *Chem. & Ind.*, 1955, (46), 1472–1473.—In paper-chromatographic separations, the preliminary equilibration of the papers with the vapours of the irrigating solvent can be considerably accelerated by moving the suspended papers, and thus moving the atmosphere, in the sealed tank. This movement can be effected by attaching small pieces of steel rod to the bottom of each paper and setting up an intermittent magnetic field by means of a coil. A circuit diagram for a chamber containing 8 tanks is described. This incorporates a micro-switch actuated by a rotating cam which allows current to pass alternately through each of two sets of four coils. S. C. I. Abstr.

1189. **Rapid surface-tension determinations using a modified pendant-drop technique.** J. A. Campbell, J. E. Christian and J. R. Eaton (Sch. of Pharm., Purdue Univ., West Lafayette, Ind., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44** (8), 501–503.—A "tangeometer" is described for measuring surface tension by the pendant-drop method. A projected image of the drop is thrown on a screen, to which is attached an adjustable square for measuring the dimensions of the drop. The method effects a time economy of about 75 per cent. over the former photographic procedure.

G. R. WHALLEY

1190. **An instrument for the rapid estimation of cross-sections of single wool fibres.** G. E. Settle (Wool Industr. Res. Ass., Headingley, Leeds, England). *J. Text. Inst., Trans.*, 1955, **46** (10), T633–T640.—An instrument is described and illustrated for quickly estimating the diameter or cross-section of single fibres. Air is drawn at constant pressure through an open slot along which the fibre is mounted, and the diameter of the fibre is read off directly from the flow meter. Standardisation of tension, calibration, accuracy and use, and applications are discussed. At the 5 per cent. probability level, the instrument will estimate wool-fibre diameter with a max. error of about $\pm 1{\cdot}30\ \mu$. For nylon the residual error is negligible.

O. M. WHITTON

1191. **A relative-humidity correction to the results of determinations of the diameter of wool fibres by the air-flow method.** S. L. Anderson (Wool Ind. Res. Ass., Headingley, Leeds, England). *J. Text. Inst., Trans.*, 1955, **46** (10), T675–T676.—In the method described, samples of wool of widely differing diameters and in equilibrium with various relative humidities were used. Correction factors have been computed to convert results of fibre-diameter determinations by the air-flow method to corresponding results at 65 per cent. R.H., *i.e.*, the atmosphere required by the standard method of using the projection microscope. O. M. WHITTON

1192. **An apparatus for estimation of nitrogen in titanium metal by the Kjeldahl steam-distillation method.** Takayuki Somiya, Kozo Momoki and Isoshi Kawashima (Univ. Tokyo, Hongo P.O., Tokyo). *Japan Analyst*, 1955, **4** (7), 440–442.—The apparatus used for steam-distillation in the Kjeldahl method was modified for the industrial analysis of titanium metal. Spherical joints were used throughout the system, and the size of each part was decreased as far as possible with decreasing accuracy. The new apparatus decreased the time taken for distillation to less than 10 min. The standard deviation is $\pm 0{\cdot}0002$ per cent. for 0·04 per cent. of nitrogen in titanium sponge, and $\pm$ 0·0004 per cent. for 0·003 per cent. of nitrogen.

K. SAITO

See also Abstract 1170.

Optical

1193. **Modified flame photometer for micro-determination of sodium and potassium.** A. K. Solomon and D. C. Caton (Harvard Med. Sch., Boston, Mass., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1849–1850.—The micro-determination of Na and K, in volumes of biological fluids of 1 μl and less, necessitated the design of a new detector for the Beckman DU flame photometer. The necessary sensitivity was obtained by the use of a photomultiplier tube (**I**) (RCA type 6217) which enabled a single detector to determine both elements. The S-10 spectral response of **I** is $\simeq$70 per cent. for Na emission at 589 mμ and $\simeq$2 per cent. (low but still usable) for K at 768 mμ. A special power supply of good regulation and stability characteristics, giving $>$800 V, is essential for use with the RCA 6217. The output from **I** is fed to a vibrating-reed electrometer which, in turn, feeds a recording potentiometer giving a pictorial record of the flame output. Samples of 0·5 ml or less can readily be used for both Na and K. D. G. HIGGS

1194. **Modified Beckman-type atomiser in the Perkin-Elmer flame photometer.** R. T. Mueller (Univ. California, Los Angeles, U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1848.—Slight modifications to a Beckman-type atomiser have resulted in improved techniques and use of smaller samples with no loss of accuracy. Little tendency to clogging was found and a more uniform rate of atomisation was obtained. The modifications include extension of the capillary inlet to 20 mm at right angles to the orifice, and reduction of the outlet orifice to half the diam. of the capillary bore; this permitted an atomisation rate of 2 to 5 ml per min. at a pressure of 10 lb per sq. in. The sample, contained in a 5-ml beaker, was held only by means of a strip spring; thus no loss in time was involved by waiting for the remainder of the soln. to be atomised. Approximate dimensions are given for the atomiser.

D. G. HIGGS

1195. **Flame photometry with standard line calibration.** R. Herrmann. *Optik*, 1955, **12** (4), 189–195.—A test solution containing Na, K and Ca is fed into the flame with a standard lithium solution. Four wavebands are selected by four filters and photocells arranged to indicate the ratios Na:Li, etc. Sensitivities are: Na, 2×10^{-10} g; K, 5×10^{-10} g; Ca, $1{\cdot}5 \times 10^{-9}$ g. Sources of error are discussed, particularly effects of varying viscosities and surface tensions of solutions. PHYS. ABSTR.

1196. **Spectrochemical analysis of solutions with the rotating-pin-electrode technique.** Á. Bardócz and F. Varsányi (Central Res. Inst. Physics, Hung. Acad. Sci., Budapest). *Acta Chim. Acad. Sci. Hung.*, 1955, **7** (1–2), 1–26.—An apparatus is described in detail in which carbon electrodes, mounted radially on a rotating horizontal shaft, dip into the soln. to be analysed. An automatic switch allows sparking or arcing only when a moistened electrode passes the counter electrode. The method should be applicable to the testing of suspensions as well as of soln. J. H. WATON

1197. **A recording micro-spectrophotometer.** P. M. B. Walker and E. M. Deeley (King's College, London). *Photoelect. Spectr. Gr. Bull.*, 1955, (8), 192–195.—A direct-reading instrument for u.v. and visible light, capable of analysing biological specimens of a few microns in length or soln. of 0·1 ml, has been designed. It is a double-beam instrument in which the light from the monochromator is passed alternately through the specimen and an optical attenuator. The two beams are finally recombined on the cathode of a photomultiplier, where they are continuously adjusted to the same intensity by a servo-mechanism controlled by the anode load of the photomultiplier. The setting of the attenuator, of log. characteristic, is proportional to the extinction. By this null method the indicated absorption is practically

independent of variations of light. A continuous spectrum from 600 to 240 mμ is provided by a 160-W high-pressure xenon arc (Osram XBO 162). A small 45° quartz prism, running on ball-bearings, is moved in and out of the light path at 50 c.p.s., directing the light alternately through the microscope and the optical attenuator; the latter is mechanically connected to the slide wire of a potentiometer-type recorder which forms the basis of the servo-mechanism. A Metrosil element is used as anode load of the photomultiplier, the loop-gain characteristics of which change only by a factor of 5, an amount sufficiently small not to affect the performance of the servo-mechanism, as the signal current in the photomultiplier changes over a range of 700 to 1. The band-width of the recording mechanism is $\simeq 1$ c.p.s., and the light energy available is sufficiently strong to give a signal to noise ratio of $\not< 100$ over the range 600 to 240 mμ. Absorption measurements on homogeneous objects were found to be proportional to specimen thickness in accordance with Beer - Lambert's law.

D. G. HIGGS

1198. **Anomalous slit-width effect in differential spectrophotometry.** C. G. Cannon (Brit. Nylon Spinners, Pontypool, Mon.). *Photoelect. Spectr. Gr. Bull.*, 1955, (8), 201–202.—Evidence is presented to show that at high extinctions the differential absorption measured varies with the slit-width used. This effect constitutes a source of error, the magnitude of which can be judged from the values quoted as apparent increased extinction. Increase of slit-width from 1·2 to 2·3 mm, at a blank extinction level of 1·0, gave $\simeq 5$ per cent. increase and, for a blank level of 1·9, 120 per cent. apparent increased extinction. Experimental techniques are discussed, but no explanation is put forward. D. G. HIGGS

1199. **Differential absorptiometry.** N. T. Gridgeman (Nat. Res. Lab., Ottawa, Canada). *Photoelect. Spectr. Gr. Bull.*, 1955, (8), 197–199.—Techniques of differential spectrophotometry, in which a standard soln. as well as that to be analysed are used, fall into two classes according to the type of instrument used. (*i*) In single-cell instruments, *e.g.*, Beckman, etc., the min. (zero) transmission scale-point is checked by "setting the dark current"; 100 per cent. transmission is then obtained by adjustment with the weaker soln. in the cell. (*ii*) In double-cell instruments, *e.g.*, the Hilger - Spekker absorptiometer, the 100 per cent. transmission is checked in the normal way against the solvent, but zero transmission is obtained by closure of the iris diaphragm over a beam that has already passed through the stronger soln. In both instances a knowledge of either the behaviour of the pure compound or the extinction coeff. of the reaction mixture is required. A further technique depends on a double-differential method that does not depend on a knowledge of the standard compound; this is discussed at some length with regard to the present limited knowledge of the errors that may be inherent in the technique. In an appendix on notation some arguments are put forward for the use of specific terms.

D. G. HIGGS

1200. **Simple short-path absorption cell.** B. F. Hochheimer and G. E. Moore (Applied Physics Lab., Johns Hopkins Univ., Silver Spring, Md., U.S.A.). *J. Opt. Soc. Amer.*, 1955, **45** (10), 891.—A simple form of absorption cell consists of a cylindrical glass body into which two circular optical windows are secured by means of wax seals. The effective cell length is determined by use of a spacer between the two windows, which may be plane or lenticular. The cell is filled through a side tube which is in register with a passage through the spacer. In the particular application which led to the design the requirements were that the path length should be of the order of 1 mm, uniform over an aperture of 35 mm diam. and known to about 1 per cent.; also the cell had to be vacuum tight and constructed of material resistant to corrosion by such gases as HCl.

B. S. COOPER

1201. **The analysis of overlapping spectral absorption bands by derivative spectrophotometry.** A. T. Giese and C. S. French (Carnegie Inst. Washington, Dept. Plant Biology, Stanford, Calif., U.S.A.). *Applied Spectroscopy*, 1955, **9** (2), 78–96.—The detection of low intensity bands when overlapped by higher intensity bands is greatly facilitated by measuring the first derivative of the transmission curve with respect to wavelength. The possibilities of the method are illustrated graphically for overlapping absorption bands of differing heights, widths and separation intervals. A recording spectrophotometer is under construction which records the derivative of the transmission curve by plotting, against wavelength, the difference between the transmittances of the absorbing material at two closely, but constantly, separated wavelengths.

P. T. BEALE

1202. **Measurement of the infra-red spectra of solids at varying temperatures by the pressed alkali halide disc technique.** R. Longworth and H. Morawetz (Polytechnic Inst. Brooklyn, N.Y., U.S.A.). *Chem. & Ind.*, 1955, (46), 1470–1471.—A cell is described in which a disc of KBr, holding a sample to be examined, is held in position in a slotted heating cylinder by a threaded collar. The cylinder is wound with a heating coil of Nichrome wire (12 ft., resistance 45 ohms per ft.), insulated with layers of asbestos tape, and varnished on the outside with a silicone - alkyd resin. The temp. is varied by changing the voltage across the cell by means of a Variac. The cell fits into a spectrometer by means of a thin slab of Kel-F. The apparatus has been used to determine the temp. dependence of the association of the carboxyl groups of a copolymer of styrene and methacrylic acid.

S.C.I. ABSTR.

1203. **Duplication of infra-red spectra on a reduced scale.** F. B. Strauss and A. E. Thompson (Dyson Perrins Lab., South Parks Road, Oxford). *Chem. & Ind.*, 1955, (44), 1402.—A slow shaft of the servomechanism of a Model 21 Perkin - Elmer double-beam spectrophotometer was coupled to the shaft of a potentiometer which supplies a voltage proportional with pen-deflection and is recorded by an independent pen-recorder. An automatically balancing potentiometer recorder was constructed from a Brown two-phase induction motor operated by a phase-sensitive amplifier, both master- and slave-potentiometer being fed from the same a.c. supply and forming part of a bridge circuit of variable ratio arms. By this mechanism, a small copy of the spectrum is supplied on a separate paper, simultaneously with the original.

S.C.I. ABSTR.

1204. **Small-grating spectrometer for the far infra-red region.** E. K. Plyler and N. Acquista (Nat. Bur. Std., Washington, D.C., U.S.A.). *J. Chem. Phys.*, 1955, **23** (4), 752–753.—Examination

of the far i.r. region has been made possible by the use of a caesium iodide prism (for wavelengths up to 50 μ) and a 7·5° refracting angle crystal-quartz prism (up to 150 μ), but the energy and resolution obtained from the latter prism was very low in the 50 to 80-μ region. Measurement beyond 50 μ was tried by replacing the Littrow mirror and prism by a small grating. Two such gratings were used, of ruled surface 2¼ in. × 3 in., with 320 and 180 lines per in., respectively. As energy detectors, thermocouples were used with a caesium iodide window for wavelengths up to 56 μ and a crystal-quartz window for the 50 to 125-μ range. Stray radiation was greatly reduced by the use of reflection gratings and reststrahlen plates; the two small plane mirrors immediately in front of, and behind, the exit slit of the spectrophotometer were replaced by plane gratings, whilst the mirror in the source box was replaced by a reststrahlen plate of NaCl, KBr or CsBr. Blackened silver mirrors, previously roughened by emery paper, may also be effectively employed to remove stray radiation and, as the quartz window of the thermocouple absorbed radiation from the range 6 to 45 μ, the second order from the grating did not overlap the first order except in the range 90 to 120 μ. With these modifications, energy can be measured in the far i.r. region with the same amplifier as for the near i.r. region.

D. G. HIGGS

1205. **Use of the (W_1W_2) diagram for X-ray spectrographic analysis.** É. E. Vaĭnshteĭn and I. D. Shevaleevskiĭ (V.I. Vernadskiĭ Inst. Geochem. and Anal. Chem., Acad. Sci. USSR, Moscow). *Zh. Anal. Khim., SSSR*, 1955, **10** (3), 184–188.—The lines used for analysis are characterised by their intensity in the form $W = \log \frac{1-T}{T}$, where T is the ratio of the amount of light passing through the emulsion to that falling on it. The (W_1W_2) diagram is obtained by plotting the W value for one line against that of another with variations in exposure conditions. The use of such diagrams in analysis, *e.g.*, of zirconium minerals, is described.

G. S. SMITH

1206. **Micro-refractometry.** P. P. Alikhanov (L. Ya. Karpov Sci. Res. Physico-Chem. Inst.). *Zavod. Lab.*, 1955, **21** (8), 964.—The refractive index of only 0·0001 ml of a liquid can be determined on the Abbé refractometer if the material is transferred by a capillary to a small piece of cigarette paper which is placed on the prism.

G. S. SMITH

See also Abstracts 952, 981, 986.

Thermal

1207. **High-temperature thermocouple. Accurate measurement of temperature up to 1880° C.** R. C. Jewell, E. G. Knowles and T. Land (The Sheffield Smelting Co., Ltd.). *Metal Ind., Lond.*, 1955, **87** (11), 217–221.—The results of work carried out on the accurate measurement of temp. above 1700° C, by means of Pt - Rh alloys containing 20 or 40 per cent. of Rh, are described. A special refractory to withstand 1900° C must be used as an outer sheath for measurements in molten steel. For calibration a special furnace was developed, in which the wires to be calibrated were placed in a tube of recrystallised alumina, heated electrically by a tungsten-wire spiral protected from oxidation by an atmosphere of pure argon. Molybdenum shields surround the tungsten, and copper shields surround the molybdenum. Such thermocouples of Rh (20 per cent.) - Pt/Rh (40 per cent.) - Pt. have shown good service for accurate measurements of temp. in the range 1700° to 1880° C.

S.C.I. ABSTR.

See also Abstracts 922, 1018, 1019.

Electrical

1208. **Zone electrophoresis on carrier substances, with a stabilised current.** W. Croon and H. Croon (Physik. Inst. Univ., Saarbrücken). *Naturwissenschaften*, 1955, **42** (15), 439–440.—When high voltages are employed, separation on the paper is often poor and deformation of the bands occurs. This is due to a rise in current, generation of heat, evaporation and resulting change in concentration of the soluble components. The supply of current is kept constant by passing it through a suitable electronic circuit. Best separation of serum-protein components for a 4 to 5-hour run was found to occur with a current flow of 5 mA.

E. KAWERAU

1209. **Ionographic isoelectric separations.** H. J. McDonald and M. B. Williamson (Stritch Sch. Med., Loyola Univ., Chicago, Ill., U.S.A.). *Naturwissenschaften*, 1955, **42** (16), 461–462.—Three half-inch filter-paper strips of Whatman No. 1 paper are employed in the conventional horizontal tank for paper electrophoresis. Two of these are put parallel to each other at 4 cm distance, but their ends dip into only one buffer compartment at opposite ends. The third strip lies across and at right angles to both these strips and the fluid that is to be analysed is applied at the centre of this strip. One buffer vessel is filled with a solution that is 1 M both to HCl and NaCl, and the other vessel with a solution that is 1 M to both NaOH and NaCl. The connecting bridge of paper is wetted with distilled water only. A potential of 450 V is applied, which results in a voltage drop of 400 V across the paper bridge. Bromophenol blue moves as a very sharp band under these conditions.

E. KAWERAU

1210. **Magnification of resolution of electrophoretic sorting patterns.** A. Kolin (Univ. Chicago, U.S.A.). *Naturwissenschaften*, 1955, **42** (12), 367–368.—A plunger that is L-shaped in cross-section is introduced into the electrophoresis cell to change the volume and shape of the chamber from the original cross-sectional area of 6 mm × 12 mm to a rectangle of 3 mm × 6 mm. This causes a widening of the bands and facilitates the removal of individual fractions through a lateral inlet in the plunger. After removal of the plunger, the laminae resume their original position. The method is particularly useful for separating substances of similar or poor mobility.

E. KAWERAU

1211. **Oscilloscopic potential measurements on the dropping-mercury electrode.** R. J. Newcombe and W. Boardman (Royal Tech. Coll., Salford, England). *Chem. & Ind.*, 1955, (46), 1473–1474.—Methods of investigating diffusive forces operative in the polarographic technique, with consequent testing of the validity of an Ilkovič-type equation, have involved current - time measurements. A technique is described by which the e.m.f. produced between the dropping-mercury electrode and the mercury pool in the "side-arm" cell is fed first to a d.c. amplifier and then on to the Y-plates of a Cossor oscilloscope. By this means, no applied voltage was used and direct measurements of voltage and

time were recorded over the life of one drop of mercury. S.C.I. ABSTR.

1212. **The reconditioning and re-calibration of glass electrodes.** S. Lewin (S.W. Essex Technical College, London). *Lab. Practice*, 1955, **4** (11), 441–443.—Methods of cleaning glass electrodes and some precautions necessary are described. The behaviour of glass electrodes that have developed a linear deviation from the hydrogen electrode function is discussed and a method of re-calibration is suggested. O. M. WHITTON

1213. **Simplified operating dead-stop magic-eye end-point indicator.** C. A. McCauley and W. J. Gresham (Monsanto Chemical Co., Monsanto, Ill., U.S.A.). *Anal. Chem.*, 1955, **27** (11),1847–1848.—The apparatus described (used in the Karl Fischer determination of moisture) incorporates a switching device to enable a number of solvent mixtures to be analysed without resetting the instrument, which is power-operated and compact, and in which the end-point indicator is a twin-beam magic-eye tube. Voltage fluctuations of up to 15 per cent. can be accommodated and all components are from common radio supplies. A selector switch introduces a resistance to the control grid of a 6SL7 valve, which is selected to compensate for differences in cell resistance for various solvent systems as compared to the cell resistance for methanol alone. A circuit diagram is given. D. G. HIGGS

1214. **Automatic differential potentiometric titrations. Electrode systems for aqueous and non-aqueous titrations.** H. V. Malmstadt and E. R. Fett (Univ. Illinois, Urbana, U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1757–1764.—An automatic potentiometric titrator has been described earlier (*Anal. Abstr.*, 1954, **1**, 3185) and details are now given of experiments conducted to extend the usefulness of the technique to non-aqueous media, and of various electrode systems most suitable for specific types of titration. The following types of titration were studied. (*i*) Acid - base in aq. soln., in which Pt (10 per cent. of Rh) and Rh *vs.* calomel electrodes gave good results. (*ii*) Organic acid - base; titration of benzoic acid with sodium methoxide in benzene - methanol soln.; good results were obtained with Pt (10 per cent. of Rh) *vs.* graphite electrodes, at a flow-rate of 2 ml per min. (*iii*) Aniline with $HClO_4$ in glacial acetic acid with electrodes as in (*ii*), at a flow-rate of 4 ml per min., a slight correction being necessary. (*iv*) Reduction - oxidation titrations involving hydrazine sulphate and KIO_3 in 4 *N* HCl, with a flow-rate of 2 ml per min. and Pt *vs.* calomel electrodes. (*v*) Pptn. reactions involving Cl' and $AgNO_3$, at a flow-rate of 7 ml per min. Good results were obtained with Pt, Pt (10 per cent. of Rh) or Ag *vs.* calomel electrodes (salt bridge used). (*vi*) Complex formation between Cl' and mercurous nitrate soln. The flow-rate used was 2·6 ml per min., with Pt, Pt (10 per cent. of Rh) or Hg *vs.* calomel electrodes. (*vii*) Multiple end-point titration, as typified by $AgNO_3$ and KCN. After the titration is automatically terminated at the first end-point, it continues to the second end-point by merely restarting the titrator by a push of a button. The flow-rate must be <3 ml per min. because of the slow equilibrium rate; platinum wire was used as an indicator electrode. D. G. HIGGS

1215. **Coulometric titrations with low-inertia integrating motor.** J. S. Parsons, W. Seaman and R. M. Amick (American Cyanamid Co., Bound Brook, N.J., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1754–1756.—A low-inertia electromechanical motor was used to integrate current and time in coulometric titrations. The permanent-magnet d.c. motor had negligible friction, low brush-contact resistance and low iron losses, with the result that speed was a linear function of applied e.m.f. The time constant of $\simeq 10$ millisec. introduces little error and, in practice, 500 stops and starts during a titration showed no difference in the results obtained. The integrator (motor) with mechanical counter was calibrated by a constant-current supply and a standard-frequency tuning-fork. An accurately measured constant current was passed through a 70-ohm resistor, across the motor, for an accurately measured time and correlated with the motor counts. The calibration factor was expressed as—

$$\frac{i\ (\text{amp.}) \times t\ (\text{sec.})}{96{\cdot}5 \times \text{counts}} = \text{milli-equiv. per count.}$$

At the 260 to 270- and 178 to 154-mA levels a difference of 0·15 per cent. in the average factor was due to a slight deviation from the linearity curve. For any given day the reproducibility of the factor was 0·1 per cent. Excellent recoveries are shown of $K_2Cr_2O_7$ by electrically produced $Fe^{\cdot\cdot}$, of the automatic titration of macro quantities of Cl' by generated $Ag^{\cdot}$, and of 0·1 milli-equiv. of acid by generated OH'. D. G. HIGGS

1216. **Precision coulometric titrator.** G. E. Gerhardt, H. C. Lawrence and J. S. Parsons (American Cyanamid Co., Bound Brook, N.J., U.S.A.). *Anal. Chem.*, 1955, **27** (11), 1752–1754.—A description is given of an instrument for coulometric titrations operated under industrial conditions with an error of <0·1 per cent. for all current values up to 450 mA. Over a period of 4 to 6 hr. at a 263-mA setting the current measurements were all well within 0·1 per cent. for all levels. A circuit diagram and details of components are given. Typical results for the titrations indicate that for $K_2Cr_2O_7$ and electrically produced $Fe^{\cdot\cdot}$ excellent recoveries can be obtained. Good performance was observed for a large number of coulometric titrations with electrically generated $Ti^{\cdot\cdot\cdot}$. D. G. HIGGS

1217. **High-frequency analysis. I. A simple heterodyne-type apparatus for high-frequency titration.** Naochika Nakamura (Takeda Pharm. Ind., Higashi-yodogawa-ku, Osaka, Japan). *Japan Analyst*, 1955, **4** (6), 345–349.—A high-frequency titrimeter of heterodyne-type was constructed; the change in frequency of the beat circuit during titration was directly measured with a micro-ammeter. The sample soln. is inserted in the grid circuit of the oscillator (2·2 megacycles per sec.). Examples of neutralisation and pptn. titrations carried out at different concn. are given and they show that the response of the apparatus becomes less sensitive below 10^{-4} *N*. K. SAITO

See also Abstracts 913, 1188.

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use in the text of an abbreviation or symbol the word is printed in full.

alternating current	a.c.
ampere	amp.
Ångstrom unit	Å
anhydrous	anhyd.
approximate, -ly	approx.
aqueous	aq.
atmospher -e, -ic	atmf.
boiling-point	b.p.
British thermal unit	B.Th.U.
calorie (large)	kg-cal.
calorie (small)	g-cal.
centimetre	cm
coefficient	coeff.
concentrated	conc.
concentration	concn.
critical	crit.
crystalline, crystallised	cryst.
cubic	cu.
current density	c.d.
cycles per second	c.p.s.
decompos -ing, -ition	(decomp.)
density	ρ
density, relative	d or wt. per ml
derivative	deriv.
dilute	dil.
direct current	d.c.
distilled	dist.
electromotive force	e.m.f.
electron-volt	eV
equivalent	equiv.
experiment	expt.
foot, feet	ft.
gram	g
gram-molecule	mole
half-wave potential	$E_{\frac{1}{2}}$
horse-power	h.p.
hour	hr.
hydrogen ion concentration	$[H^{\cdot}]$
hydrogen ion exponent	pH
inch	in.
infra-red	i.r.
insoluble	insol.
kilogram	kg
kilovolt	kV
kilowatt	kW
maxim -um, -a	max.
melting-point	m.p.
microcurie	μC
microgram	μg
microlitre	μl
micron	μ
milliampere	mA
millicurie	mC
milligram	mg
millilitre	ml
millimetre	mm
millimicron	mμ
millivolt	mV
minimum	min.
minute (time)	min.
molar (concentration)	M
molecul -e, -ar	mol.
normal (concentration)	N
number	no.
observed	(obs.)
ounce	oz
part	pt.
patent	pat.
parts per million	p.p.m.
per cent. wt. in wt.	per cent. w/w
per cent. wt. in vol.	per cent. w/v
per cent. vol. in vol.	per cent. w/v
potential difference	p.d.
pound	lb
precipitate	ppt.
precipitated	pptd.
precipitating	pptg.
precipitation	pptn.
preparation	prep.
qualitative, -ly	qual.
quantitative, -ly	quant.
recrystallised	recryst.
refractive index	n_λ
relative humidity	R.H.
revolutions per minute	r.p.m.
saponification value	sap. val.
saturated calomel electrode	S.C.E.
second (time)	sec.
soluble	sol.
solution	soln.
specific gravity	sp. gr.
specific rotation	$[\alpha]_\lambda$
square centimetre	sq. cm
standard temperature and pressure	s.t.p.
temperature	temp.
ultra-violet	u.v.
vapour density	v.d.
vapour pressure	v.p.
volt	V
volume	vol.
watt	W
wavelength	λ
weight	wt.

In addition the following symbols are used—

greater than	$>$	less than	$<$
not greater than	$\ngtr$	not less than	$\nless$
is proportional to	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P., or D.A.B., together with the identifying numeral.

Radicles are represented by the usual symbols; positive ions have superscript dots and negative ions superscript dashes, *e.g.*, $Cu^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, Cl', SO_4''. Metals that exist in more than one valency state are represented by their symbols with appropriate superscript roman numerals, *e.g.*, ferric iron becomes Fe^{III} and cuprous copper Cu^{I}.

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